Synthesis of New Alkyn-1-ylsilanes.

1,1-Organoboration,

1,2-Hydroboration

Dissertation

Zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften (Dr. rer. nat.) an der Fakultät für Biologie, Chemie und Geowissenschaften der Universität Bayreuth

Vorgelegt von

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Ezzat Khan

Dedicated to my

Parents

ABBREVIATIONS AND SYMBOLES

Å	Angstrom
Abb	Abbildung (German)
br	broad
b. p.	boiling point
9-BBN	9-borabicyclo[3.3.1]nonane
Bu	n-butyl
^{t}Bu	tertiary butyl
BuLi	n-Butyl lithium
BEt_2	diethylboryl group
BPr_2	dipropylboryl group
°C	degree celsius
°	degree
d	doublet
dd	doublet of doublet
ddd	doublet of doublet of doublet
dt	doublet of triplet
Et	ethyl
g	gram
h	hour
Hz	Hertz
INEPT	**I**nsensitive **N**uclei **E**nhanced by **P**olarisation **T**ransfer
J	coupling constant (Hz)
K	Kelvin
m	multiplet
mg	milligram
min	minute
mL	millilitre
mmol	millimole
m. p.	melting point
M	molecular weight (g/mol)
Me	methyl, $-CH_3$
MHz	megahertz

n. o.	not observed
n. m.	not measured
NMR	**N**uclear **M**agnetic **R**esonance
ppm	**p**arts **p**er **m**illion
Pr	*n*-propyl
Ph	phenyl
q	quartet
r. t.	room temperature
R	organyl group
s	singlet
t	triplet
vgl	vergleiche (German)

The respective coupling constants in the text are represented as below,

( )	$^{n}J(^{1}H,X)$, X = ^{29}Si, $^{119/117}Sn$ and $^{n}J(^{1}H,^{1}H)$
[ ]	$^{n}J(^{13}C,^{29}Si)$
{ }	$^{n}J(^{13}C,^{119}Sn)$
[( )]	$^{n}J(^{29}Si,^{119}Sn)$
[[ ]]	$^{n}J(^{119/117}Sn,^{119/117}Sn)$

1. INTRODUCTION

1.1. Boron and Silicon in general

Boron was isolated in 1808 by Sir Humphry Davy, Gay-Lussac and Thenard. It was identified as element in 1824 by Berzelius[1] although, its compounds have been known for thousands of years. Boron is a lustrous grey-black colored material, always contaminated with carbon and/or nitrogen. Various boron-oxygen compounds occur in rocks and soil (average concentration of 10-20 ppm) and it is considered to be the second hardest element.[2] Boron possesses two naturally occurring isotopes ^{10}B (19.78 %) and ^{11}B (80.22 %). It belongs to Group 13 of the Periodic Table, with outer $2s^2$, $2p^1$ electronic configuration. In most of its compounds, it prefers to be three-coordinated (sp^2 hybridized), with trigonal planar geometry, or four-coordinated with tetrahedral surroundings in the presence of a suitable electron donating group.[3-6] Organoboron compounds have widespread biological applications[7] for example, composites of antifouling agents or in medicine for treatment of cancer and diabetes. Since 1980s, some important reactions such as haloboration[8,9] or Suzuki-Miyaura couplings,[10] boron-containing polymers[11] and potential applications of phosphorus-boron compounds[12,13] have been noted. The reactivity of boron might be related to, (a) a vacant p_z-orbital; (b) small atomic radius (0.08-0.095 nm) and small relative atomic mass (10.811); (c) relatively high electronegativity (2.01 Mulliken) if it is considered as a metal.[2]

Silicon is the next important heteroelement used in this work and is the second most abundant element (27.70 %) in the earth crust.[14] Gay Lussac and Thenard prepared impure amorphous silicon in 1811. In pure form it was prepared by Berzelius in 1824 and in crystalline form by Deville in 1854. Crystalline silicon has metallic lustre and greyish color. It belongs to Group 14 with outer electronic configuration $3s^2$, $3p^2$. It is usually four-coordinated (sp^3 hybridized) and is tetrahedrally surrounded. Typically, the silicon coordination number can be increased to five and six in the cases of Lewis-acidic silanes.[15] Some of the five-coordinated silicon compounds are more reactive[16] towards nucleophilic attack as compared to its four-coordinated analogues. Silicon-element bonds are known for a great variety of elements, metals and non-metals. The bonds of particular importance are, Si-Si, Si-C, Si-O, Si-N and Si-Metal.[17] It plays a major role in modern electronics as a semiconductor. Silicon compounds have many applications, e.g. polysiloxanes (“silicones”) are used as oil, grease, rubber and resins.[18,19] They are resistant to

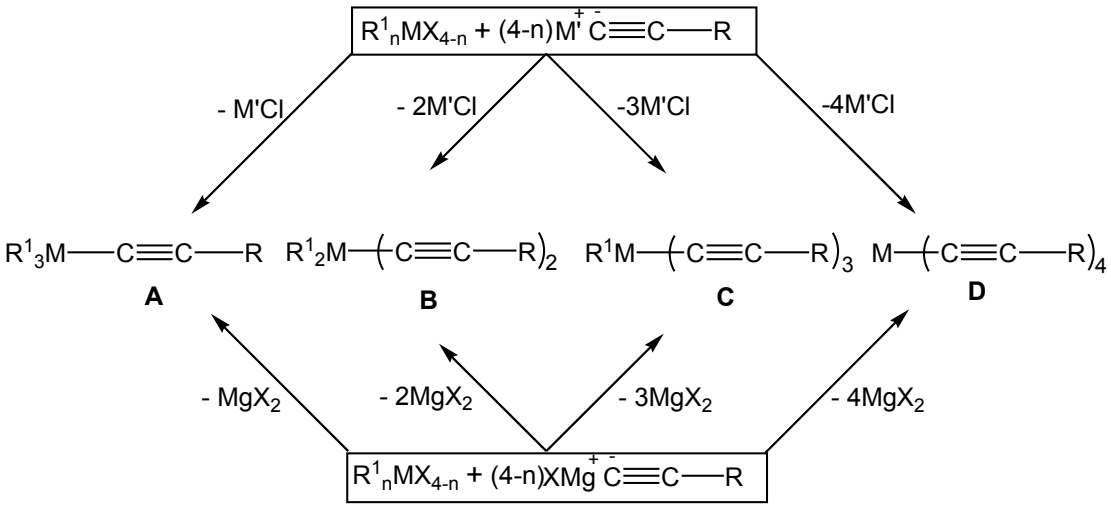
heat and water and are non-conducting materials. Silicon polymers,[20] aminopropyl terminated polydimethylsiloxane are heat-resistant and serve as raw materials for ceramics. Poly(divinylsiloxyethylene glycol) is oxygen (O_2) and photo-resistant and can be used in electronic devices. Owing to their chemically unique and robust nature, silicones have been applied in pharmaceuticals *e.g.*, in rubber tubes, contact lenses, artificial lungs and blood storage containers[2] to name just a few examples.

Numerous compounds containing boron and silicon have been studied. They have promising properties and are well known to material scientists. They possess excellent thermochemical stability.[21] Polymers containing silicon, boron, carbon and nitrogen (Si-B-C-N) are converted into protective coatings at high temperature[22] and are molecular precursors for Si-B-C-N ceramics.[23] Compounds containing both of these elements have been used in many reactions for designing more advanced materials. Because they offer remarkable attractions to chemists, since (a) they have similar chemistry;[24] (b) they have suitable NMR active isotopes (^{11}B (I = 3/2) and ^{29}Si (I = ½)) allowing to monitor reactions by ^{11}B or ^{29}Si NMR spectroscopy at any stage and intermediates can be proposed; (c) interpretations of NMR spectra are straightforward, frequently based on ^{13}C-^{29}Si (spin-spin coupling satellites) ^{11}B-^{13}C (broad ^{13}C NMR resonance signals of carbon atom attached to ^{11}B); (e) most of the starting materials used are relatively cheap and easily available.

1.2. Alkyn-1-ylsilanes

One of the first alkyn-1-ylmetal compounds with a main group element, was Me_2As-C≡C-$AsMe_2$, described by H. Wieland, in 1923.[25] He used the Grignard reagent BrMg-C≡C-MgBr and in principle, alkyn-1-yl-Group 14 compounds can be prepared in a similar way by the reaction of alkali metal acetylides, Li-C≡C–R, Na-C≡C–R, K-C≡C–R or acetylenic Grignard reagents, XMg-C≡C–R with the respective metal halides.[26-28] A general reaction for the preparation of Group 14 alkyn-1-yl compounds is shown in Scheme 1.1. Only silicon-containing compounds called alkyn-1-ylsilanes will be discussed, since they were used in performing this work. Many of the alkyn-1-ylsilanes are fairly stable towards air and moisture and can be stored without decomposition for long periods of time.[29] Nevertheless, the compounds represented in Scheme 1.1 are quite reactive. This reactivity is due to Si-C≡ bond polarity which in turn depends on the electronegativity of the carbon atom attached to silicon. This concept can already be seen if we compare the C-H acidity

in hydrocarbons as a function of the nature of the C-C bond. The group electronegativity of the organyl rest increases with the s-character of the hybrid orbital used by the carbon atoms. Thus, the electronegativity reaches a maximum for sp hybridized carbon (3.29, Mulliken) as compared to sp^3 (2.48, Mulliken) and sp^2 (2.75, Mulliken) hybridised carbons.[30] Clearly, the Si-C≡ bond is polar and reactive owing to the group electronegativity of the -C≡C- moiety.



Scheme 1.1. General synthetic route for the preparation of some alkyn-1-yl Group 14 compounds, where M = Si, Ge and Sn; M´ = Li, Na, K; R and R^1 = H, Me, Bu, ^{t}Bu, Ph; and X = Cl, Br. This dissertation contains only alkyn-1-ylsilanes (M = Si).

Alkyn-1-yl Group 14 compounds of type **A–D**, (Scheme 1.1) are attractive starting materials for organometallic synthesis. They can be converted *via* 1,1-organoboration or 1,2-hydroboration into novel alkenes, dienes, allenes and heterocyclic dienes.[29]

In organometallic synthesis alkyn-1-ylsilanes have been used for the preparation of σ-alkynyl[31] and π-alkyne[32,33] complexes. Moreover, alkyn-1-ylsilanes have also been used in resins[34] and even as rocket fuels.[35] The alkyn-1-ylsilanes bearing other functionalities on Si atom, especially H and Cl, offer attractive properties. They have been used for M-Si bond formation[36,37] and sometimes the -C≡C- bond[37-39] also participates in the reaction. Apparently, the reactivity of alkyn-1-ylsilanes as ligands depends on the nature of the metal as well as the alkynyl group of the silanes. The alkynyl unit acts as η^1 or η^2 ligand in these complexes.

A positive aspect of alkyn-1-ylsilanes is their easy handling and availability. For the present work mono-, di-, tri-, and tetraalkyn-1-ylsilanes were prepared by the reaction of alkynyl lithium with respective chlorosilanes. Generally this method afforded mixtures for silanes bearing more than one Si-Cl functions. For synthesis of monoalkyn-1-ylsilanes the mixture contained the desired products and other alkyn-1-ylsilanes, in which more than one Si-Cl function(s) were substituted by alkynyl groups. Formation of highly pure (≈ 95-100%) mono-substituted products was not observed. However, the concentration of di-, tri- or tetraalkyn-1-ylsilanes as side products can be controlled by applying various methods; *e. g.,* reasonably high yield was obtained by adding 4-8 fold excess of the respective chlorosilane at –78 °C.[26,28] In a similar way tri- and tetraalkyn-1-ylsilanes were synthesised by using the alkynyl lithium in slight excess and adding the trichloro- or tetra(chloro)silane at low temperature (-78 °C), followed by heating of the reaction mixture at 40 °C for 2-3 h.[40] Further purification of the desired alkyn-1-ylsilanes required fractional distillation under reduced pressure or recrystallization using an appropriate solvent.

1.3. Methods of characterization

The alkyn-1-ylsilanes have been studied and characterized by various techniques,[32,41,42] although a complete NMR spectroscopic data set is missing in most cases. The silanes serving as starting materials for this work were fully characterized by ^{13}C, ^{1}H and ^{29}Si NMR spectroscopy (Figure 1.1). In some cases single crystals suitable for X-ray diffraction were achieved and studied in solid state by the same technique.

The alkyn-1-ylsilanes bearing up to four Si-C≡C- functions were converted *via* 1,2-hydroboration and/or 1,1-organoboration into a number of novel silanes. Some new compounds such as, alkenylsilanes, 1-silacyclobutenes, 1-chloro-1-silacyclopent-2-enes, spirosilane(silacyclobutenes and silacyclopent-2-enes), borolenes and siloles, were obtained. All these compounds were characterized by multinuclear NMR spectroscopy (^{1}H, ^{11}B, ^{13}C, ^{29}Si and ^{119}Sn) and some single crystals suitable for X-ray diffraction were studied in solid state and X-ray structures were determined.

Multinuclear NMR spectroscopy provides a wealth of information and it was possible to monitor the progress of reactions and determine some solution state intermediates. Also with the help of this technique, the complete reaction mechanism

in several cases was fully explored (Figure 1.2). The X-ray single crystal data could be collected for some crystalline materials. Structural determination of some silicon-containing heterocycles for example, 1-silacyclobutene, 1-chloro-1-silacyclopent-2-ene, spirosilanes (silacyclobutene and silacyclopent-2-enes) and borolenes in the solid state were the ever first examples of such types of compounds.

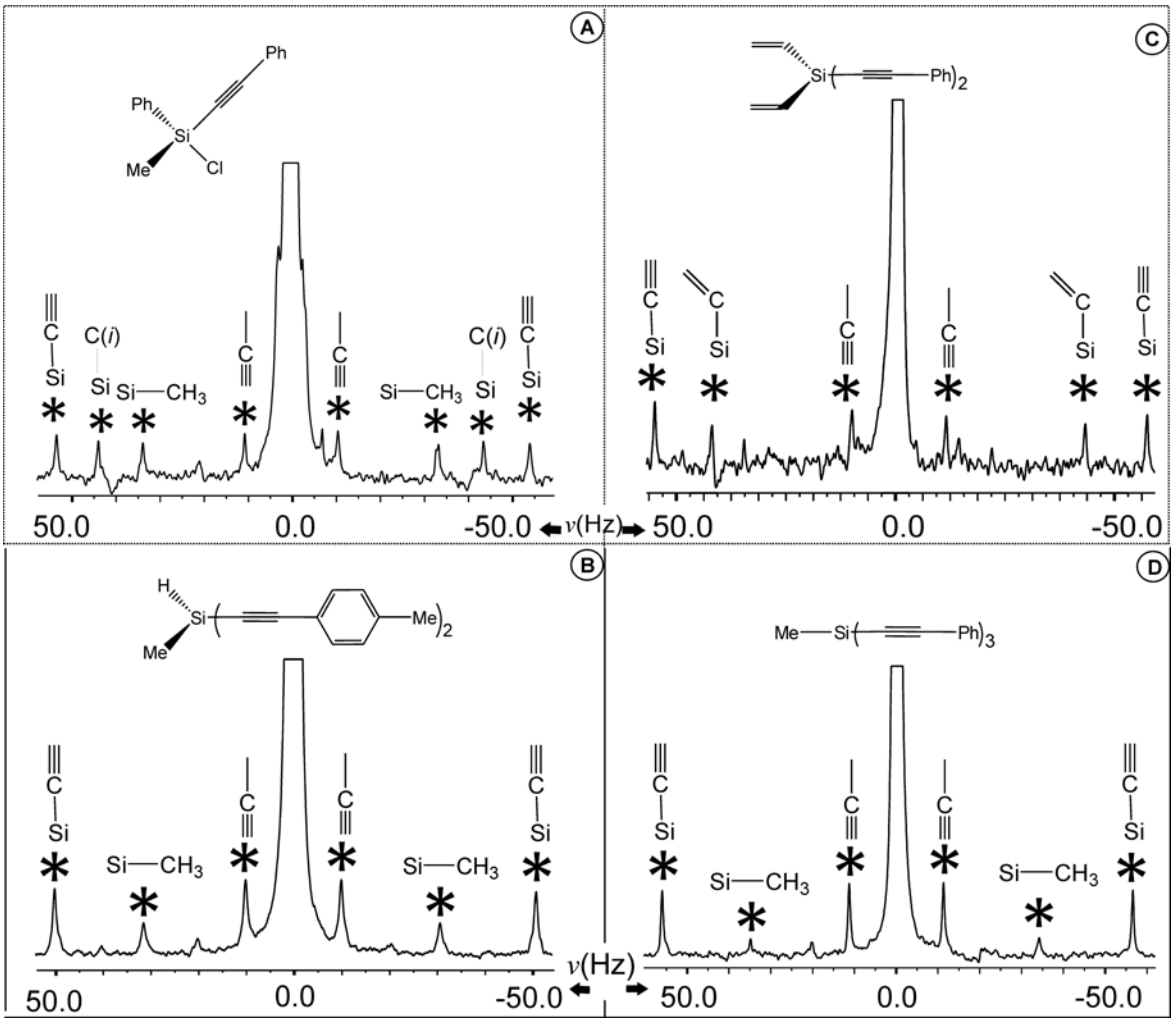


Figure 1.1. Expansions of $^{29}Si\{^{1}H\}$ NMR spectra of some of the starting silanes bearing one, two and three alkyn-1-yl functions. The satellites marked by asterisks, correspond to the coupling constants $J(^{13}C,^{29}Si)$.

1.4. 1,2-Hydroboration of alkyn-1-ylsilanes

It is conceivable that the α-carbon atom in alkyn-1-ylsilanes possesses greater electron density ($Si^{\delta+}$-$C^{\delta-}$≡C-). This nucleophilic carbon atom is a favourable soft centre for attack by boron as the electrophilic centre of a boron hydride. Hence, a hydroborating reagent (Et_2B-H or 9-BBN) reacts selectively with alkyn-1-ylsilane to link the boryl group to the α-carbon next to silicon and the hydrogen (B-H) becomes

bonded to the β-carbon. These reactions are called 1,2-hydroboration reactions. The 1,2-hydroboration[43] reactions are well known to take place under various conditions.[44] In the case of alkyn-1-ylsilanes, the products contain the boryl and silyl groups linked to the same olefinic carbon atom[45–47] (Scheme 1.2). Such compounds of type **F** are readily available by the reaction of alkyn-1-ylsilanes with hydroborating reagents. The reactions are highly selective with few exceptions.[44,46a,48] The time required to induce 1,2-hydroboration depends on the respective substituents both on the silicon atom and the Si-C≡C- bonds. Apparently, the reactivity is reduced by Si-Cl function(s), since the 1,2-hydroboration of alkyn-1-yl(chloro)silanes requires either stirring at room temperature for several days or heating the reaction mixture at 60 - 80 °C for few hours if hexane is used as solvent.[45] Attempts have been made to study hydroboration of alkyn-1-ylsilanes bearing only one Si-Cl function.[45,49,50] Analogous reactions for alkyn-1-yl(trichloro)silanes and alkyn-1-yl(dichloro)silanes have not been studied so far.

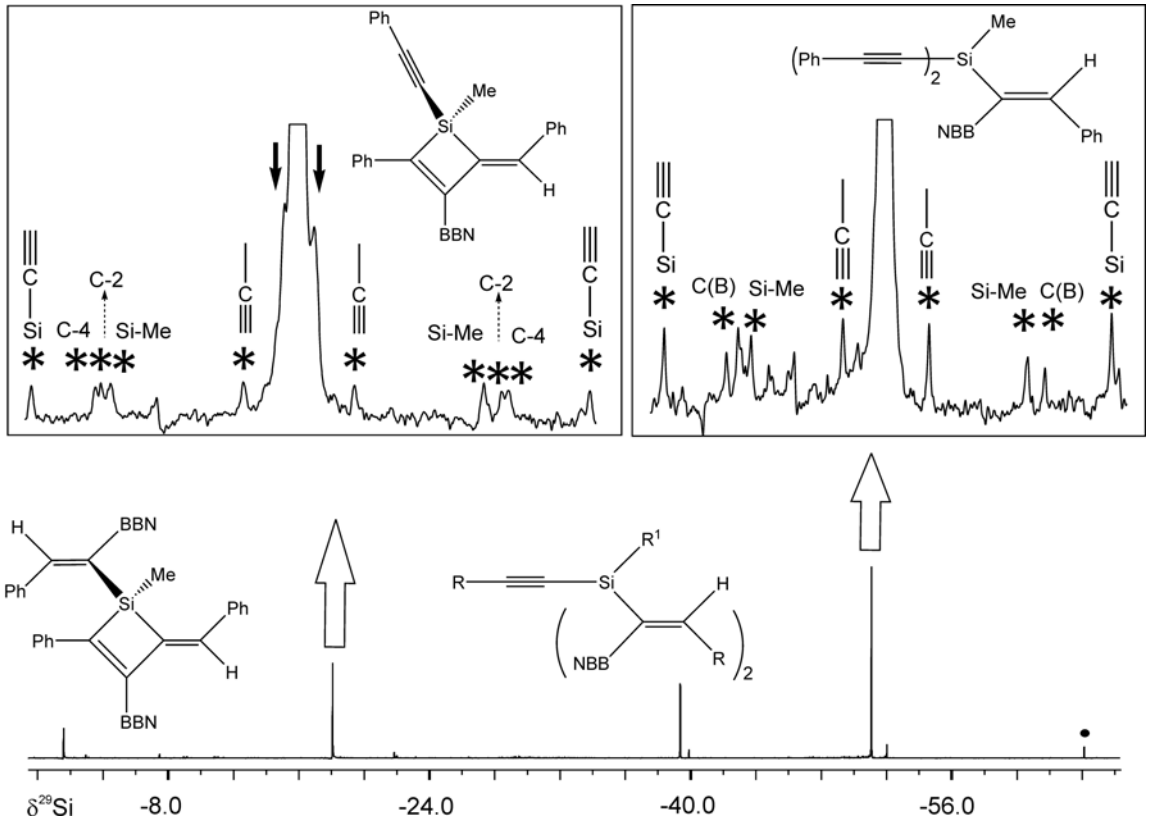
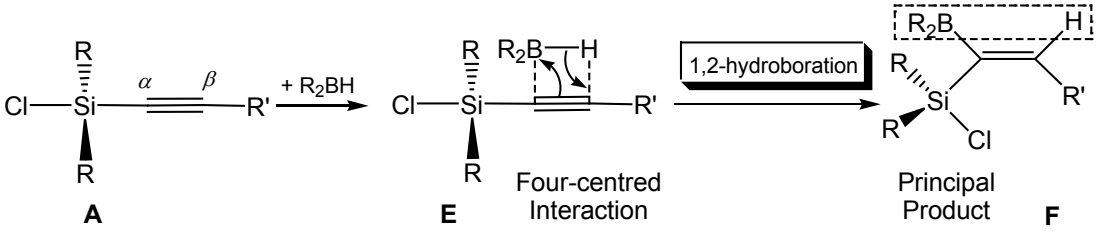


Figure 1.2. $^{29}Si\{^{1}H\}$ NMR spectra of the reaction mixture (lower trace, in initial stages and upper inserted, after reaction completion) representing all important intermediates and final products. Starting silane is marked by black circle. Expansions shown with satellites marked by asterisks, correspond to the coupling constants $J(^{13}C,^{29}Si)$.

In this dissertation 1,2-hydroboration of alkyn-1-yl(chloro)silanes using 9-borabicyclo[3.3.1]nonane, 9-BBN, as hydroborating reagent have been studied exclusively. Considering silanes containing up to three Si-Cl functions, it was aimed to get the expected results including information on solid state structures.



Scheme 1.2. General representation of 1,2-hydroboration reaction where R_2B = Et_2B-H, 9-BBN or any other diorganoboryl group. The marked region on product side denotes addition of new groups.

The alkyn-1-yl(trichloro)silanes, alkyn-1-yl(dichloro)silanes and alkyn-1-yl(dichloro)(vinyl)silanes were treated with triorganoboranes, BEt_3 and BPr_3 under harsh reaction conditions (heating at 100 - 120 °C for several days). The results obtained were surprising as far as BEt_3 is concerned, since for the first time, 1,2-hydroboration instead of 1,1-organoboration was observed.

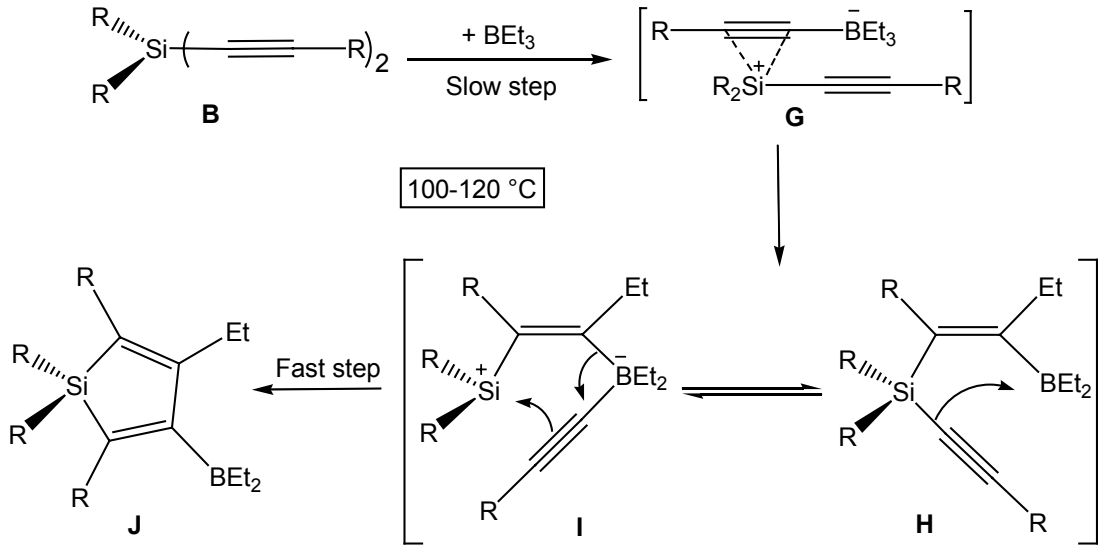
1.5. 1,1-Organoboration of dialkyn-1-ylsilanes

The 1,1-organoboration of monoalkyn-1-ylsilanes has been reported[51] using various triorganoboron compounds. By studying the reactivity of alkyn-1-ylsilanes bearing two and three Si-Cl functions towards triorganoboranes, a different behaviour was observed. As mentioned above, 1,2-hydroboration occurred, an unprecedented and completely new finding for triethylborane, BEt_3. The main emphasis in this section is on 1,1-organoboration reactions of di- and trialkyn-1-ylsilanes with the well known organoborating reagent BEt_3. The products afforded by 1,1-organoboration of silanes bearing two or more alkyn-1-yl groups with BEt_3 are commonly known as siloles (1-sila-2,4-cyclopentadienes).

Recently, siloles have attracted greater attention owing to their unique reactivity, photophysical and electron transporting properties.[52 - 56] They have been prepared by numerous different synthetic routes including 1,1-organoboration of dialkyn-1-ylsilanes.[29,57 - 61] Preparation of siloles *via* 1,1-organoboration is more versatile, if

compared with other preparative methods.[52,62 - 65] The advantage of this method is its simplicity and the variety of substituents to be introduced at all ring positions including the silicon atom.

At high temperature one Si-C≡C bond is activated in the presence of BEt_3. In first step cleavage of one Si-C≡C bond leads to a short-lived alkyn-1-ylborate-like zwitterionic intermediate of type **G**, shown in Scheme 1.3. Intermediate **G** rearranges to another short lived alkyn-1-ylsilane of type **H** or borate-like intermediate **I**. Both of these intermediates are in equilibrium with each other and further intramolecular 1,1-vinylboration leads to the final product **J** (silole). The first intermolecular step of the reaction is slow and requires heating at 80 - 100 °C for several hours to several days.[66,67] Under the same reaction conditions in the second step, which is comparatively fast, the intermediates of type **H** and **I** can not be detected almost in all of these reactions. In the final step intramolecular 1,1-vinylboration causes ring closure (siloles **J**).



Scheme 1.3. General reaction mechanism for synthesis of siloles including intermediates.

In the course of this dissertation, a number of silole derivatives were prepared *via* 1,1-organoboration, with different functional groups at the Si atom, like Si-C=C, Si-C≡C-, Si-Cl and Si-H. The behaviour of all these functional groups was studied and some fruitful information regarding reactions were extracted. Thus, silanes bearing Si-Cl functions react slowly in the presence of BEt_3, and some silanes ($Cl_2Si(C{\equiv}C\text{-}Bu)_2$ and $R^1(Cl)Si(C{\equiv}C\text{-}Ph)$, R^1 = Me, Ph) afforded 1-silacyclobutenes as

a result of 1,2-hydroboration caused by Et_2BH produced *in situ*. The silanes bearing Si-H function are comparatively more reactive and the reactions proceed *via* 1,1-organoboration. The possible variation of groups at the silicon (Si-C≡C-, Si-Cl and Si-H) provoked for studying and comparing the reactivity of Si-vinyl in the presence of two Si-C≡C- groups [$(H_2C=CH(R^1)Si(C\equiv C\text{-}R)_2$, $(H_2C=CH)_2Si(C\equiv C\text{-}R)_2$, where R = Bu, Ph and R^1 = Me, Ph]. The data revealed clean formation of siloles and the 1,1-ethylboration left the Si-vinyl function untouched.

1.6. Combination of 1,2-hydroboration and 1,1-organoboration

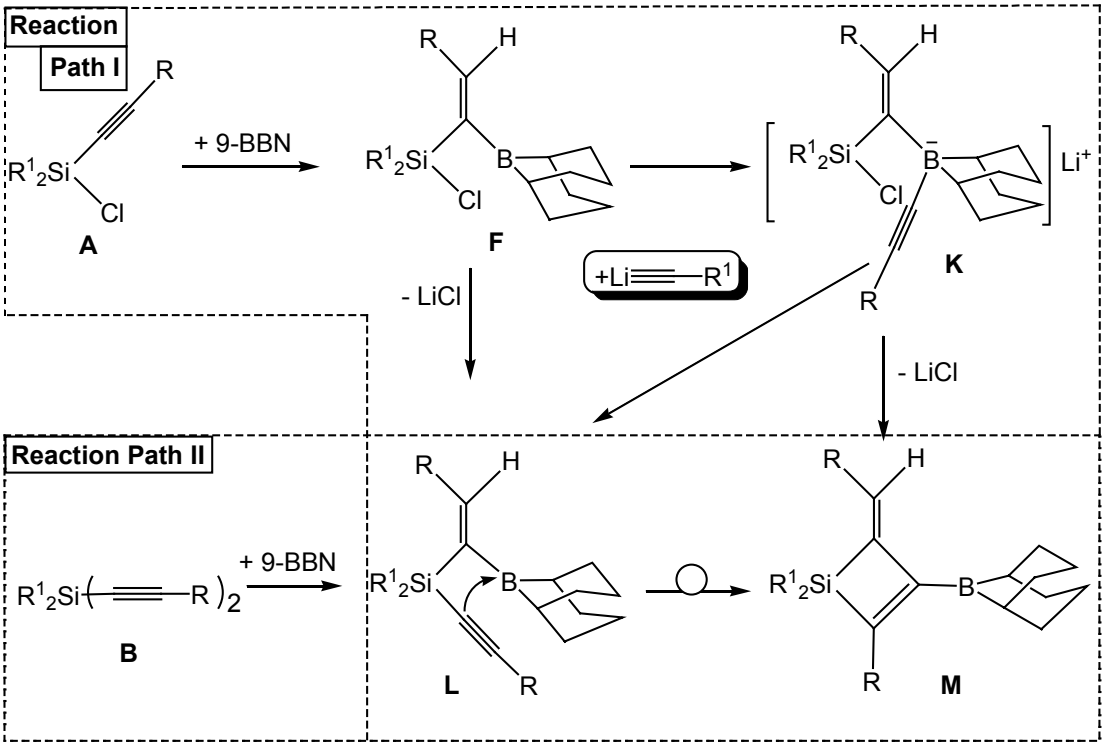
Intermolecular 1,2-hydroboration[44 - 48] and intermolecular 1,1-organoboration[29] are two reactions requiring totally different conditions. The former get complete either at room temperature or after heating at 80 - 100 °C for a couple of hours, whereas the latter requires prolonged periods of heating at 100 - 120 °C[29] and its success depends on the respective substituents both on silicon and on the Si-C≡C- bond. An intramolecular 1,1-organoboration reaction is expected to require much less stringent conditions. Therefore, the boryl group has to be introduced into the molecule for example by 1,2-hydroboration in order to allow for an easy and fast intramolecular 1,1-organoboration of an additional Si-C≡C-R function. This combination of quite different boration reactions has proved successful in the synthesis of various new heterocycles e.g. 1-silacyclopent-2-enes[68,69] and 1-silacyclobutenes.[70] The reaction mechanism for the synthesis of 1-silacyclobutenes is shown in Scheme 1.4. Some of the intermediates such as **L** have already been detected in reaction solutions.[70] The rearrangement proceeds *via* a borate-like intermediate[29] as in **K**. Cleavage of the Si-C≡C- bond and formation of the B-C≡C bond leads to a borate and finally to the product **M**.

Using the concept of combining 1,2-hydroboration and 1,1-organoboration, the missing information (NMR data regarding intermediates and solid state structure) related to 1-silacyclobutenes could be deduced. For the synthesis of novel spirosilane (silacyclobutenes), the same concept was used and all the required information were extracted.

1.7. Reactivity of novel boryl-substituted Si-containing compounds

The boryl-substituted (alkenyl)silanes are useful synthons for further transformations. They can be converted into, alkenes,[71 - 73] silicon containing hetero-cycles[74] and allenes[75] (some examples are shown in Scheme 1.5). The boryl-

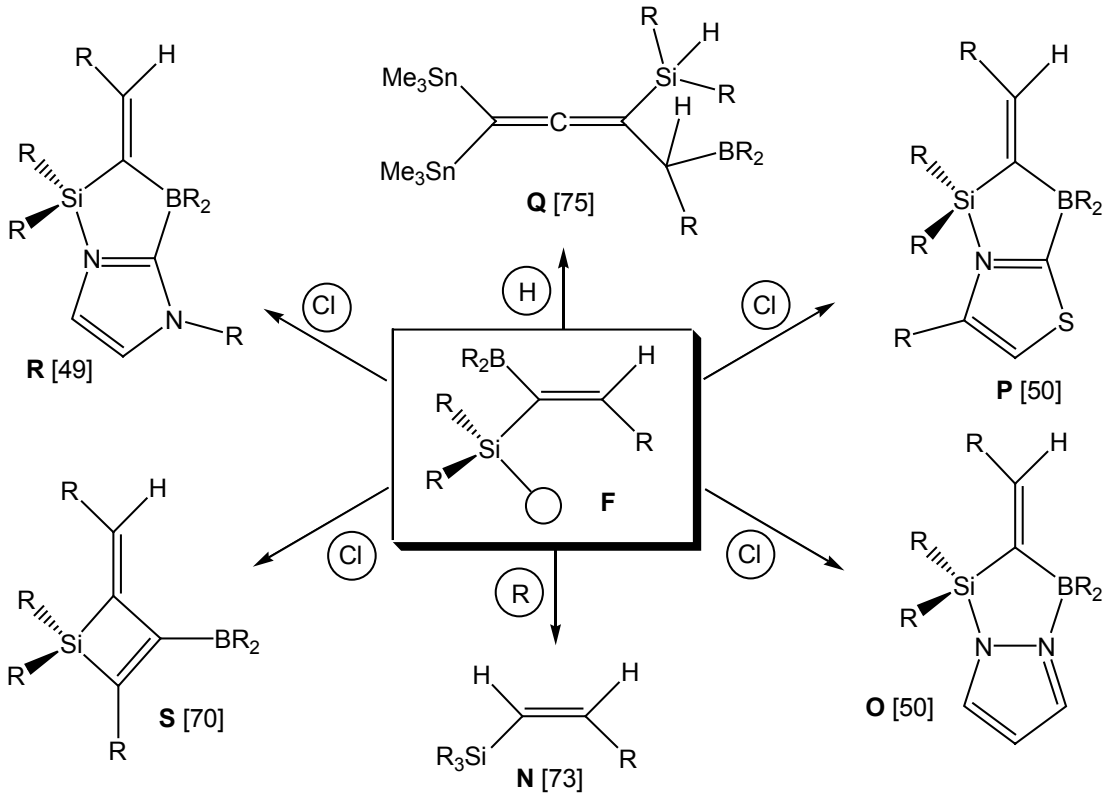
substituted alkenes, possessing Cl_3Si-, $Cl_2(R^1)Si$- or $Cl_2(H)Si$- moiety give promising results. Borolenes are formed in reactions with bis(trimethylstannyl)ethyne. Besides this function the role of -C≡C-Ph and -C≡C-Bu groups was also considered. In this context, for the first time some reactions were carried out, where in some cases the product distribution depended upon the groups R = Ph or Bu of Si-C≡C-R. The alkenes $Cl_3Si(9\text{-BBN})C{=}C(H)R$ (R = Bu, Ph) and $Cl_2(R^1)Si(9\text{-BBN})C{=}C(H)Ph$ (R^1 = Me, Ph) afforded clean formation of borolenes while the silanes $Cl_2(R^1)Si(9\text{-BBN})C{=}C(H)Bu$ (R^1 = Me, Ph) gave mixture containing allenes and borolenes.



Scheme 1.4. Formation of 1-silacyclobutene derivatives by combining intermolecular 1,2-hydroboration and intramolecular 1,1-organoboration

Among boryl-substituted heterocyclic silanes, the reactivity of siloles is of particular importance. Some reactions of siloles with acetylene dimethyldicarboxylate, tetracyanoethene,[76,77] dialkyn-1-ylsilanes,[66] acetic acid,[45,60,78,79] water,[60,71] and ethanolamine[59] have been studied. In these reactions either more advanced heterocycles by [4+2]cycloaddition, simple protodeborylated compounds, or other substituted products[80] have been obtained. Much attention has been paid to deborylated products and the boron containing side products have previously been discarded as water soluble waste materials or simply neglected. Different conditions for protodeborylation reactions have been outlined, ranging from mild reaction

temperature[45,78,79] to boiling of the respective boryl-substituted silane[68] in an appropriate solvent.



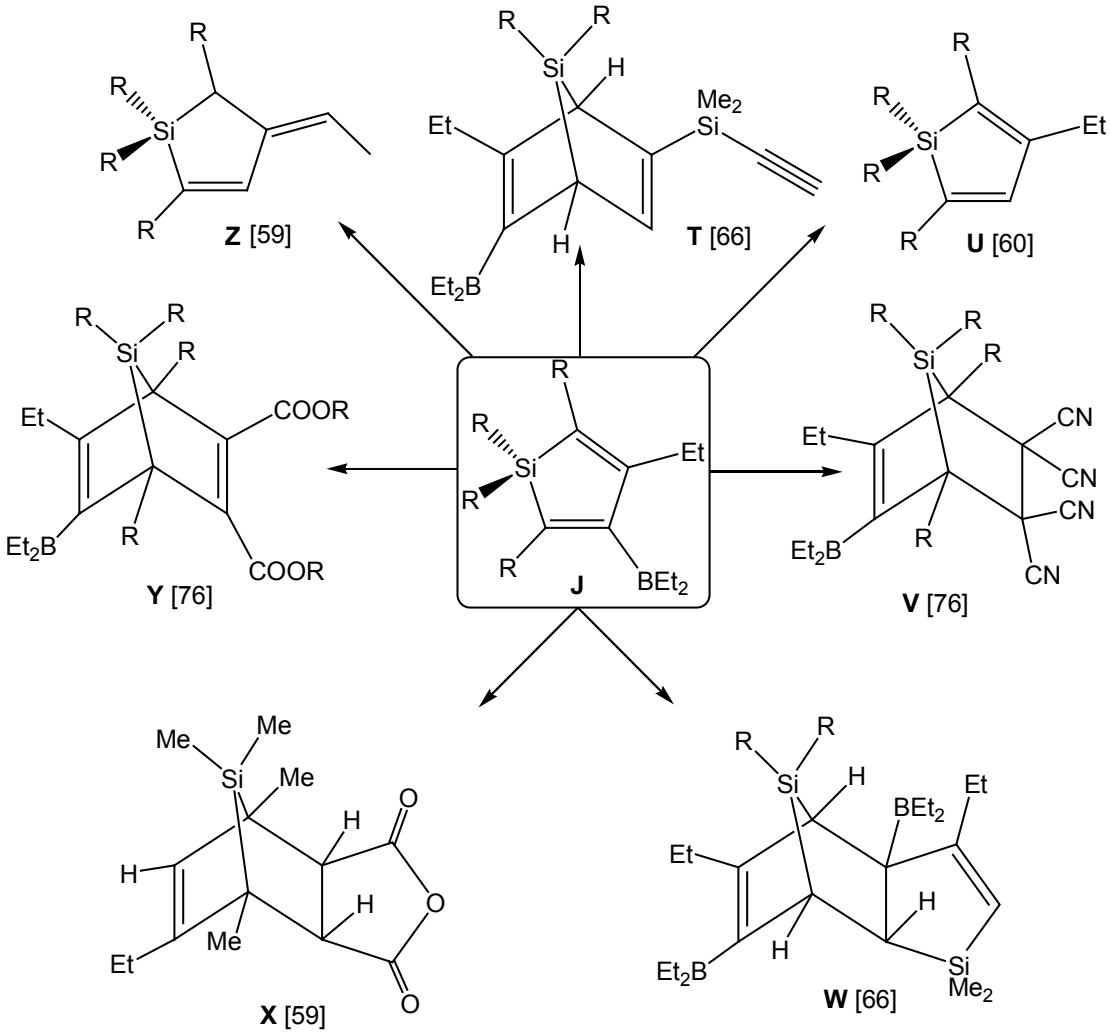
Scheme 1.5. Various new systems developed by exploiting the reactivity of boron-substituted alkenysilanes. The group encircled is explained for each starting alkenylsilane. For more details see corresponding references.

1.8. Goals and achievements

One among the main goals was to fully characterize the starting alkyn-1-ylsilanes by NMR spectroscopy and X-ray crystal structural analysis where possible. To explore their reactivity towards diorganoboron hydride, 9-BBN and triorganoboranes, BEt_3 and BPr_3, was the next focus. For the first time the hydroboration capability of BEt_3 just like the well established hydroborating reagent 9-BBN has been explored and discussed.

Current interest lies in the combination of 1,2-hydroboration and 1,1-organoboration. For the first time it was used for the synthesis of novel 1-silacyclobutenes in 2003.[70] But information such as, solid state structure and solution state NMR data of intermediates regarding 1-silacyclobutenes were missing. The alkyn-1-ylsilanes were converted into 1-silacyclobutenes and all the missing

information was obtained. This idea was developed in its advanced form for the synthesis of spirosilane(silacyclobutenes).



Scheme 1.6. Some new compounds obtained from the reactions of siloles as starting materials with various other reagents.

The reactions of the synthesized compounds bearing boryl groups were studied with various reagents. Slow hydrolysis, oxidation and conversion of alkenes into borolenes, protodeborylation and synthesis of oxasilaboratoles were the main achievements in this work. The important systems of novel compounds are summarized in Figure 1.3.

In all the compounds discussed in the next chapters 2 - 7 of this dissertation, the organyl groups on Si- atom R^1 are defined for each series of compounds in their respective schemes and the substituents R (Si-C≡C-R) are denoted by bold, small letters as suffix of the respective number. Several suffixes were used for representing

different groups, intermediates and nature of reactions. They are listed below in Table 1.1.

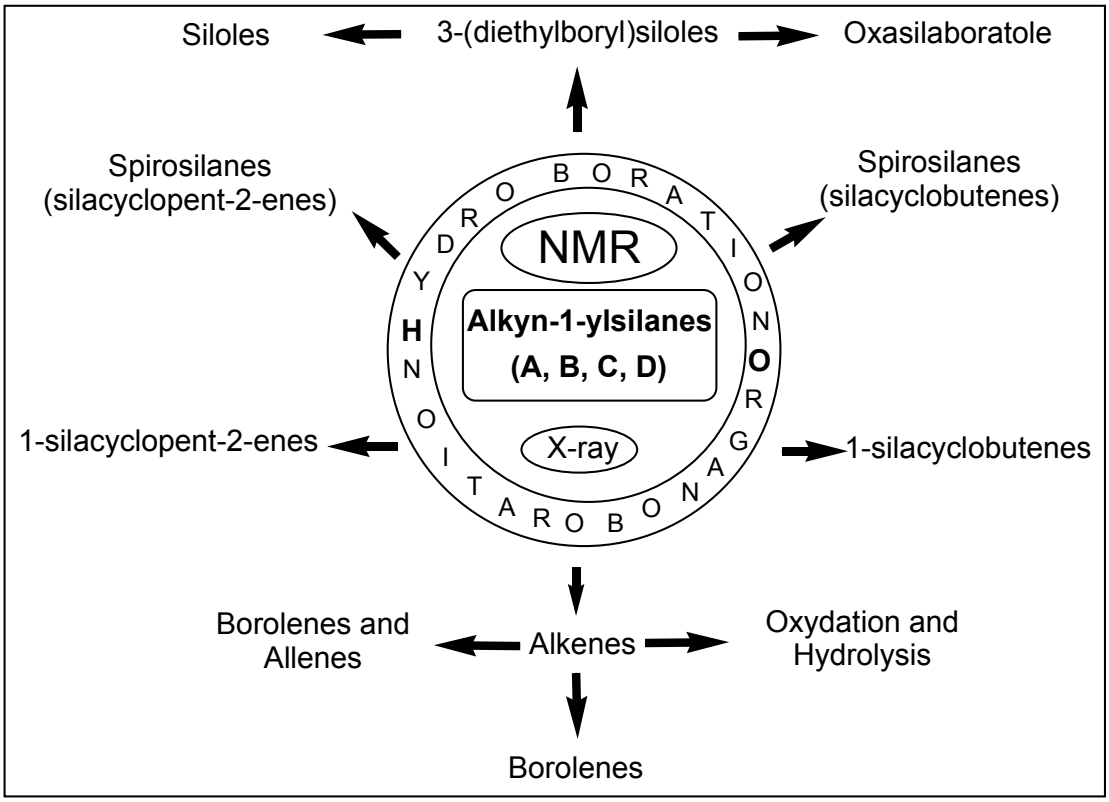


Figure 1.3. Diagrammatic representation of the results obtained.

Table 1.1. Organyl substituents on Si-C≡C- group and their representation

Suffix	Remarks	Description of groups
a	One or more ≡C-Bu groups in the molecule	Bu (C_4H_9)
b	One or more ≡C-^{t}Bu groups in the molecule	^{t}Bu (C_4H_9)
c	One or more ≡C-Ph groups are present	Ph (C_6H_5)
d	One or more ≡C-(4-Me-C_6H_4) groups	4-Me-C_6H_4 (C_7H_7)
e	One or more ≡C-(4-^{t}Bu-C_6H_4) groups	4-^{t}Bu-C_6H_4 ($C_{10}H_{13}$)
-i	Intermediate not detected in reaction solution	--
-P	Protodeborylated compound	--

2. NEW ALKYN-1-YLSILANES

The alkyn-1-ylsilanes are useful starting materials for many transformations. During the course of this dissertation they were converted into boryl-substituted alkenes and various heterocycles *via* the well known process of 1,2-hydroboration, 1,1-organoboration and combining of 1,2-hydroboration and 1,1-organoboration (Figure 1.3). The number of alkyn-1-yl groups on silicon atom is the key function to the products, and the silanes bearing different number of alkyn-1-yl groups afforded different products on reaction with hydroborating or organoborating reagents. On the basis of further reactivity starting silanes were divided into six categories.

i. Monoalkyn-1-yl(chloro)silanes
ii. Monoalkyn-1-yl(vinyl)silanes
iii. Dialkyn-1-ylsilanes
iv. Dialkyn-1-yl(vinyl)silanes
v. Trialkyn-1-ylsilanes
vi. Tetraalkyn-1-ylsilanes

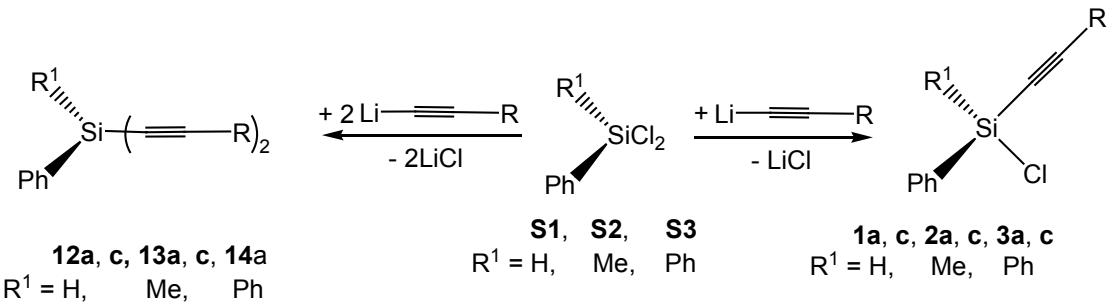
Syntheses and characterization of all these silanes are discussed in this chapter and their further reactivities are outlined in more detail in the next chapters (3 - 7).

2.1. Monoalkyn-1-ylsilanes

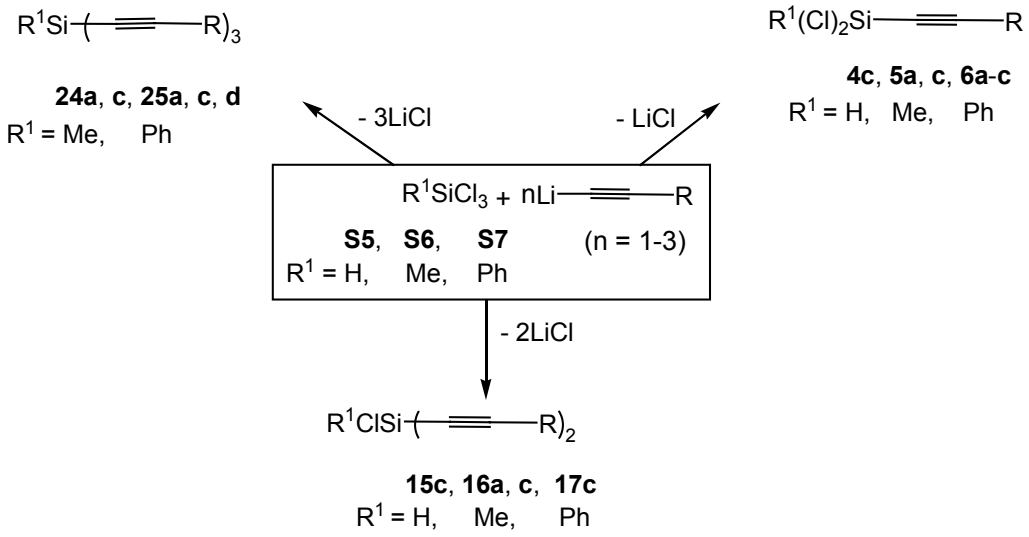
Monoalkyn-1-yl(chloro)silanes were prepared following the literature procedure[26 - 28] by the reaction of freshly prepared alkynyl lithium with the corresponding chlorosilanes. Generally such reactions lead to mixtures containing the desired silanes accompanied by other fractions where more than one Si-Cl function is substituted. The formation of such side products can not be avoided completely, however, the yield of monoalkyn-1-ylsilanes can be increased considerably if a large excess (four- to eightfold) of respective chlorosilane at low temperature (-78 °C) is used.

The synthesis of alkyn-1-ylsilanes bearing up to three Si-Cl functions was achieved during the period of this dissertation. They were prepared in pure form and were studied by multinuclear NMR spectroscopy (^{13}C, ^{1}H and ^{29}Si). The work was initiated by treating commercial dichlorosilanes with the alkyn-1-yl lithium (Scheme 2.1). These silanes afforded two products, monoalkyn-1-yl(chloro)silanes (principle product, 60 - 70%) and dialkyn-1-ylsilanes ($R^1PhSi(C{\equiv}C\text{-}R)_2$) as a side products. Both of the products were separated by fractional distillation (Figure 2.1). The related

NMR data (^{13}C and ^{29}Si) are summarized in Table 2.1 and ^{1}H NMR data in Experimental section.



Scheme 2.1. Synthesis of (alkynyl-1-yl)(chloro)silanes, dialkyn-1-ylsilanes and their separation.

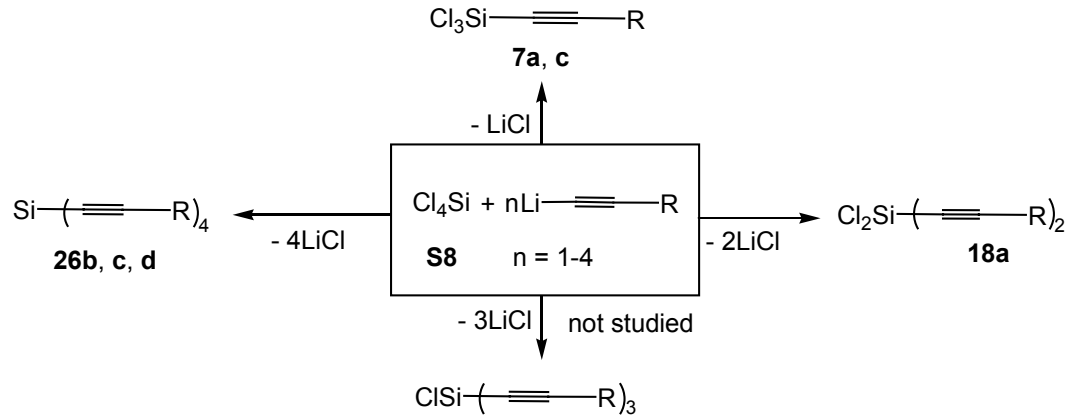


Scheme 2.2. Simultaneous formation of silanes bearing -Si(C≡C-R), -Si(C≡C-R)$_2$ and -Si(C≡C-R)$_3$ functional groups.

The prime interest was to introduce inorganic functional groups on the silicon atom *e.g.*, Si-H and Si-Cl functions. The number of Si-Cl functions was increased gradually and a second series of monoalkyn-1-ylsilanes bearing two Si-Cl functions were prepared in the similar way as described above. The starting silanes possess three Si-Cl replaceable functions (Scheme 2.2) facilitating three products, hence the yield of the desired silanes, **4 - 6** to be recovered becomes lower (30 - 35%) if compared with silanes, **1 - 3**. Pure samples of the alkyn-1-yl(dichloro)silanes **4 - 6** for further studies were obtained by fractional distillation.

The number of side products increases with the increase in Si-Cl functions. The tetrachlorosilane affords four products (Scheme 2.3) on reaction with alkyn-1-yl

lithium. The silane was added slowly in eightfold excess and the reaction was allowed to take place at low temperature i.e. –78 °C. The desired silanes (Cl_3Si-C≡C-R, R = Bu, Ph) were formed in 25 - 30 %, accompanied by other silanes (*e.g.,* $Cl_2Si(C{\equiv}C\text{-}R)_2$, $ClSi(C{\equiv}C\text{-}R)_3$ and $Si(C{\equiv}C\text{-}R)_4$). Fractional distillation was fruitful for the purification of these silanes **7a** and **7c.** They were isolated in pure state and used for further studies.



Scheme 2.3. Syntheses of alkyn-1-yl(chloro)silanes, obtained as a mixture in the reaction.

NMR spectroscopy

Some of the detailed information regarding syntheses, characterization and chemical reactions of the alkyn-1-ylsilanes have been reported.[41,80] Unfortunately the NMR data set is either incomplete or has not been determined at all.[81,84] Therefore, these compounds were considered for full characterization and a complete NMR data set was collected. The NMR data (^{13}C, ^{29}Si) related to the series of monoalkyn-1-ylsilanes **1 - 7**, are listed in Table 2.1 and Table 2.2. The ^{13}C(Si-C≡C) signals are found within the expected range: the Si-$^{13}C{\equiv}$ signal appears in the range of δ = 76.2 ppm (**6b**) – 88.2 ppm (**2c**) and the ≡^{13}C resonance signals were observed in the range of δ = 107.8 ppm (**6c**) – 121.8 ppm (**6b**). The range is typical for main group element alkynyl substituted-compounds.[41] All other ^{13}C NMR signals belonging to R and R^1 are in the expected range. The coupling constants $^1J(^{13}C,^{29}Si)$ expectedly become larger with increase in the number of Si-Cl functions. The smaller $^1J(^{13}C,^{29}Si)$ value, 107.8 Hz was observed for **2c** (Cl(Me)PhSi-C≡C-Ph) and the maximum value, 177.6 Hz for the same type of coupling constant was observed for **7a** (Cl_3Si-C≡C-Bu). Both the silanes **2c** and **7a** possess one and three Si-Cl

functional groups, respectively. In some cases the coupling constants were also confirmed from ^{13}C satellites appearing in ^{29}Si-NMR spectra (Figure 2.1 upper insert).

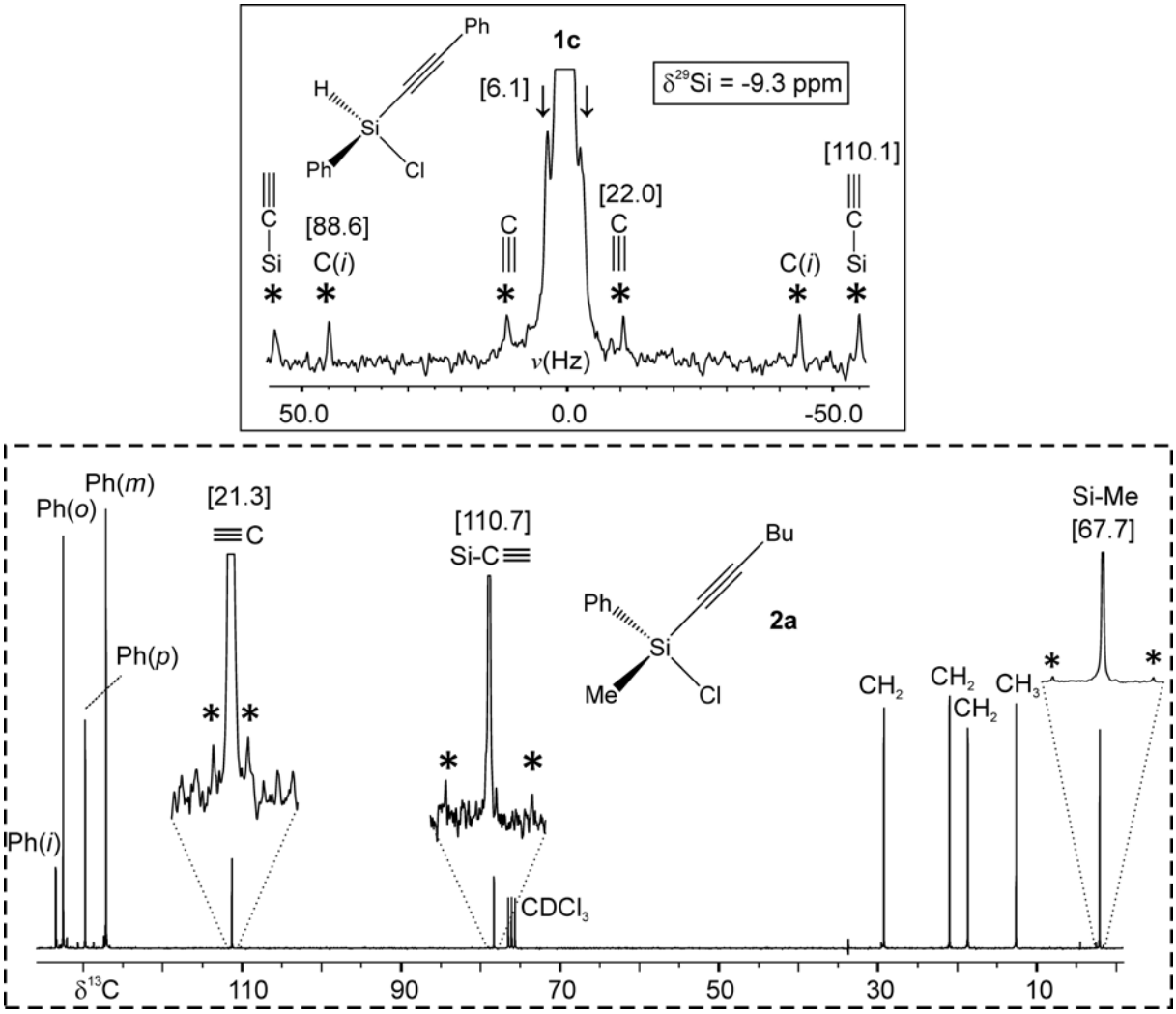


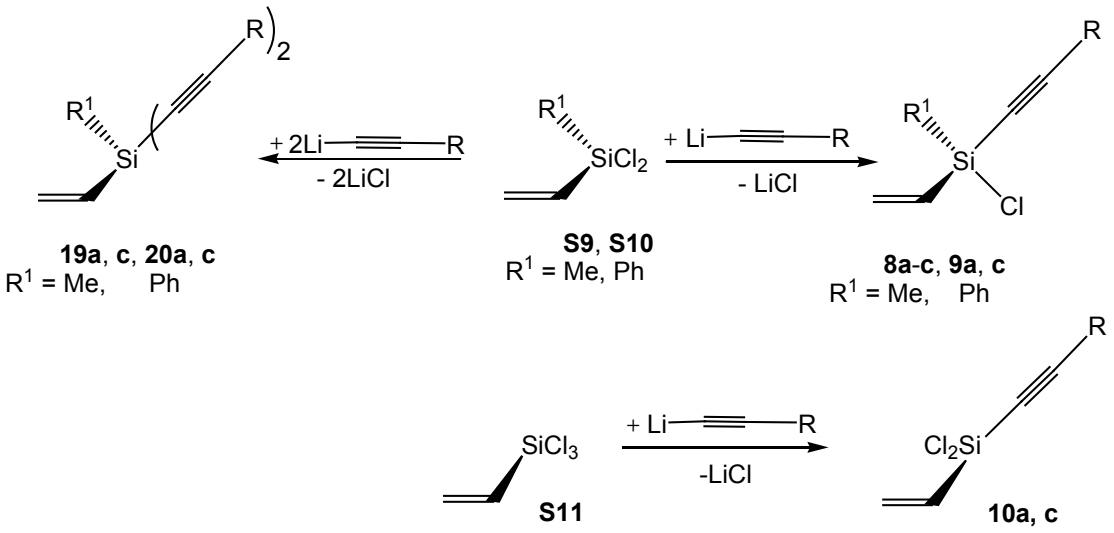
Figure 2.1. 59.6 MHz $^{29}Si\{^1H\}$ NMR spectrum (upper insert) of the Chloro(phenylethynyl)(phenyl)silane **1c** and 75.8 MHz $^{13}C\{^1H\}$ NMR spectrum (lower) of the chloro(hex-1-yl)(methyl)(phenyl)silane **2a** solution in $CDCl_3$. Expansions are given for the signals showing ^{13}C and ^{29}Si satellites respectively, marked by asterisks, correspond to $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$ spin-spin coupling constants. Further satellites are visible close to the parent signal in ^{29}Si of **1c**, (6.1 Hz) arise due to $^nJ(^{13}C,^{29}Si)$ where n ≥ 2.

The ^{29}Si NMR data show that resonance signals of respective silanes are in the expected range as reported for some analogous silanes (-0.4 ppm for $Cl(Me_2)Si$-C≡C-CH_2-NH_2 and –22.6 ppm for Cl(Me)(H)Si-C≡C-CH_2-NH_2).[67,85] The NMR

parameters of these silanes (Table 2.1and Table 2.2) are in full agreement with the proposed structures.

2.2. Monoalkyn-1-yl(vinyl)silanes

Having a variety of substituents (Cl, H, Me and Ph) on silicon atom, the next focus was to introduce a simple unsaturated group (vinyl) on silicon atom. It was expected in the light of previous experience that the reactions will work well for achieving these silanes in pure form. To characterize them by multinuclear NMR spectroscopy and to use them as starting materials in further reactions were the next considerations. For this purpose alkyl(dichloro)(vinyl)silanes (alkyl = Me, Ph) and trichloro(vinyl)silanes were treated with alkynyl lithium, (Scheme 2.4) in the same way as discussed for silanes **1 - 7**. The desired silanes were formed in reasonably good yield (ca. 70 %). The side products, $Me(H_2C{=}CH)Si(C{\equiv}C\text{-}R)_2$, $Ph(H_2C{=}CH)Si(C{\equiv}C\text{-}R)_2$, $Cl(H_2C{=}CH)Si(C{\equiv}C\text{-}R)_2$ and $(H_2C{=}CH)Si(C{\equiv}C\text{-}R)_3$, were isolated by conventional fractional distillation under reduced pressure. The method of distillation was useful and pure samples were obtained which were used for further reactions (Figure 2.2 shows a representative ^{13}C spectra of **10a**).



Scheme 2.4. Syntheses of alkyn-1-yl(vinyl)silane derivatives.

NMR spectroscopy

A complete set of NMR data (^{13}C, ^{1}H, ^{29}Si) for the title silanes (**8 - 10**) was collected in Table 2.3 and Experimental part. The data set is consistent with the proposed structures and well comparable with that of the previously discussed silanes **1 - 7**. The substituent effect of the vinyl group, upon coupling constants and

silicon chemical shift, is almost identical to a phenyl group. For example, in silane Me(Cl)(H_2C=CH)Si(C≡C-Bu), **8a**, the ^{29}Si chemical shift was observed at -12.8 ppm while silane Me(Cl)(Ph)Si(C≡C-Bu) **7a** exhibits a chemical shift for the same nuclei at -10.4 ppm. Similarly the ^{29}Si chemical shift for Ph(Cl)(H_2C=CH)Si(C≡C-Bu) **10a**, is -21.9 ppm while -20.0 ppm was observed for the silane Ph_2(Cl)Si(C≡C-Bu), **8a**. The ^{29}Si chemical shifts of the silanes with Si-Ph and Si-vinyl functions differ from each other by ± 2 ppm, if the rest of the environment is identical.

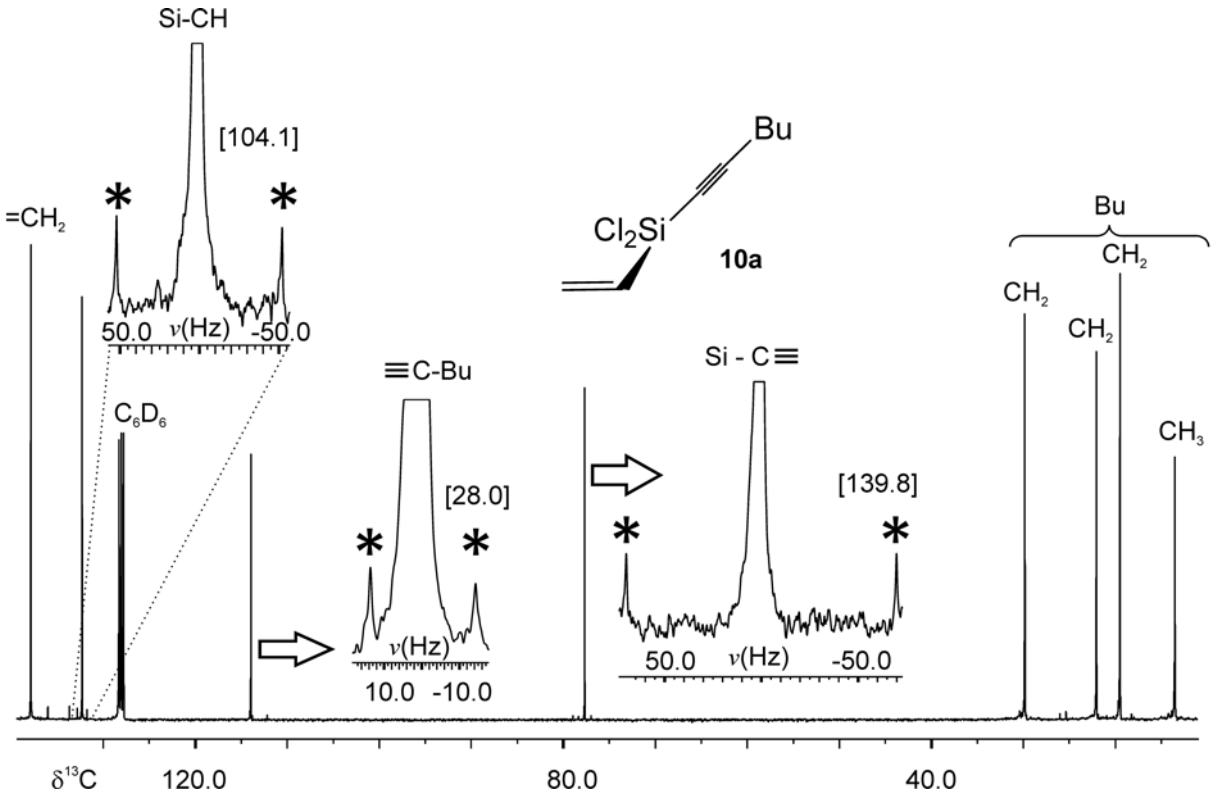
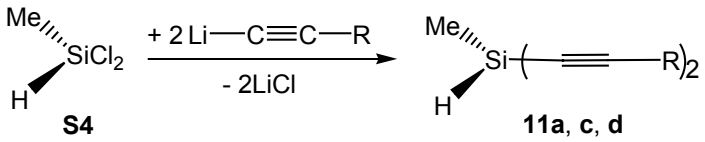


Figure 2.2. 100.4 MHz ^{13}C{^{1}H} NMR spectra of dichloro(hexyn-1-yl)(vinyl)silane **10a** (solution in C_6D_6). Expansions are given for the signals show ^{29}Si satellites corresponding to $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$ spin-spin coupling constants.

2.3. Dialkyn-1-ylsilanes

The dialkyn-1-ylsilanes have been prepared[89] following a different synthetic procedure, by dehydrogenative coupling of terminal alkynes in the presence of ytterbium-imine complex as the catalyst. The well known experimental procedure of reacting alkynyl lithium with respective chlorosilanes was adopted for the syntheses of dialkyn-1-ylsilanes studied in this work. These silanes **12 - 18** were side products accompanying silanes **1 - 7**, were purified by fractional distillation and collected as

second fraction from the respective mixtures. In some cases a second distillation was required to achieve the desired purity (Figure 2.3). The next focus was to study these side products. They are regarded as useful precursors for heterocyclic compounds. It was interesting in many aspects (economic, less time consuming, environment friendly) to use the side products for useful purposes.



S4 **11a**, **c**, **d**

Scheme 2.5. Reaction of dichloromethylsilane with twofold alkyn-1-yl lithium.

Pure dialkyn-1-ylsilanes **11a**, **c** and **11d**, were prepared by the reaction of two equivalents of alkynyl lithium and one equivalent of dichloro(methyl)silane at 0 °C (Scheme 2.5). The reaction mixture was warmed to room temperature and heated at 40 °C for 30 min.[40] The solid materials were separated and all volatiles were removed. The desired products were obtained in excellent yield (90 - 95 %). Normal procedure (distillation **11a**, **11c** or crystallization **11d**) was applied for purification and pure samples were isolated (Figure 2.3).

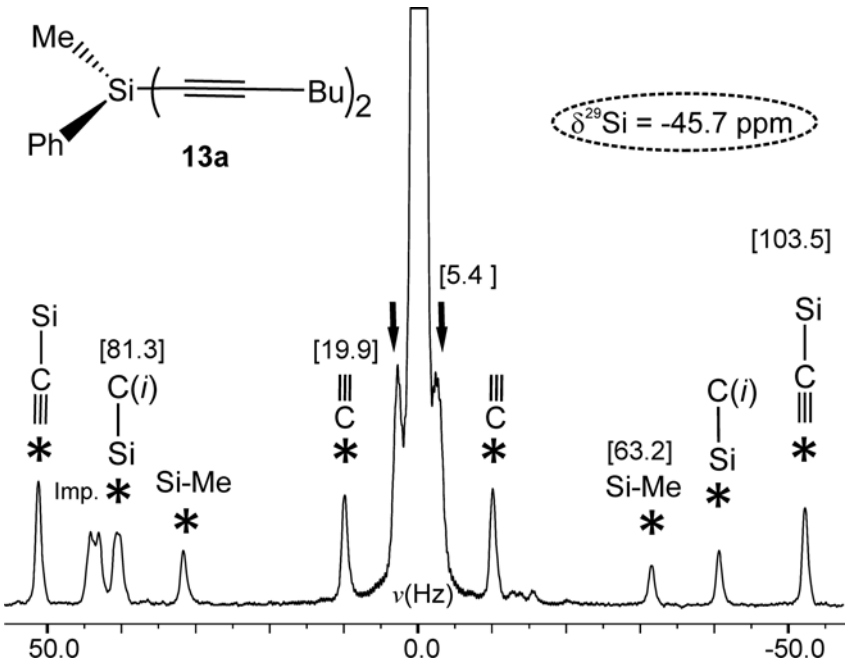


Figure 2.3. 59.6 MHz $^{29}Si\{^{1}H\}$ NMR spectra of di(hexyn-1-yl)(methyl)(phenyl)silane **13a** in C_6D_6. Expansion is given for the parent signal shows ^{13}C satellites, representing coupling constants $^{1}J(^{13}C,^{29}Si)$ and $^{2}J(^{13}C,^{29}Si)$. Satellites closed to parent signal, marked by arrows indicates coupling over ≥ 2 bonds.

The molecular weight of alkyn-1-ylsilanes increases with the increase in the number of -C≡C-R groups, making the boiling point of the respective silanes higher. This situation makes the purification of desired silanes difficult. Also considering them as side products in previous reactions, their formation was suppressed as much as possible. In most of the cases, twofold distillation was helpful to get pure samples (Figure 2.3). Owing to the above stated reasons, all these silanes were not achieved in proper sequence (Table 2.5). Anyhow some of them were obtained in reasonable purity (90 - 95 %), studied by multinuclear NMR spectroscopy and used in further transformations.

NMR spectroscopy

The NMR data (^{13}C and ^{29}Si) belonging to dialkyn-1-ylsilanes, **11 - 18** are given in Table 2.4 and Table 2.5. The NMR data (chemical shifts δ^{13}C, δ^{1}H, coupling constants $J(^{13}C,^{29}Si)$ and $J(^{1}H,^{29}Si)$) compare well with those of reported silanes[77,80,85] and are consistent with silanes **1 - 10**. The ^{13}C NMR signals of the ethynyl carbon atoms can be assigned without any difficulty. The assignments are strongly supported by $^{1}J(^{13}C,^{29}Si)$ and $^{2}J(^{13}C,^{29}Si)$ spin-spin coupling constant values. All the ^{13}C NMR signals belonging to 'R' groups are within the expected range.

The ^{29}Si chemical shifts show a gradual change in frequency from higher field to the lower field. The δ^{29}Si data for the desired silane are found in the range of -32.7 ppm (**16a**) to -65.5 ppm (**12a**). ^{29}Si NMR spectroscopy is an important technique used throughout for determining the composition of mixtures, and the coupling values $J(^{13}C,^{29}Si)$ obtained from ^{13}C NMR were confirmed from ^{13}C satellites in ^{29}Si NMR spectra in many cases. The ^{29}Si NMR spectra presented in Figure 2.3 and Figure 2.4 provide clear evidence of this statement.

The ^{1}H NMR data for the said silanes are given in Experimental part. The relative intensities of signals indicating number of protons in different groups are helpful in confirming the proposed structures. The δ^{1}H data differ slightly (ca. ± 0.5 ppm) from monoalkyn-1-ylsilanes **1 - 7**. The ^{1}H(Si-Ph. Ph) NMR signals were observed as multiplets in the aromatic region and were not assigned to respective protons.

*X-ray structural analysis of methyl-di(phenylethynyl)phenylsilane **13c***

The molecular structure of **13c** is shown in Figure 2.5 together with selected bond lengths and angles. The data pertinent to crystal structure refinement and solution are given in Table 2.6. It crystallizes in the space group P2(1)/c. Surprisingly crystal structures of such simple dialkyn-1-ylsilanes as **13c** are not reported. Some related compounds are known, bearing $R_2Si(C{\equiv}C\text{-})$ units (R = Me, Pr, Ph), either bonded to another Si-C≡C- unit making cyclotriynes[87] or being bonded to a metal centre.[31] All the bond lengths and angles are in close agreement with $Ph_2Si(C{\equiv}C)_2$, $Pr_2Si(C{\equiv}C)_2$ units of cyclotriynes,[87] $Ph_2Si(C{\equiv}CH)(\text{-}C{\equiv}C\text{-M})$ unit of Os and Ru alkynyl complexes[31] and a dialkyn-1-yltin[88] analogue. In the crystal structure of **13c**, the Ph ring (C11 - C16) is twisted by 62.1° against C3 - C8 plane. The geometry around the silicon atom is distorted tetrahedral, all C-Si-C angles are different. They are of three types, close to tetrahedral angle (∠ C1-Si1-C17 = 109.6°), smaller (∠ C1-Si1-C9 = 107.5°) and wider (∠ C9-Si1-C18 = 110.1° and ∠ C17-Si1-C18 = 112.1°) than ideal tetrahedral angles. Intermolecular or intramolecular interactions were either negligible or not observed.

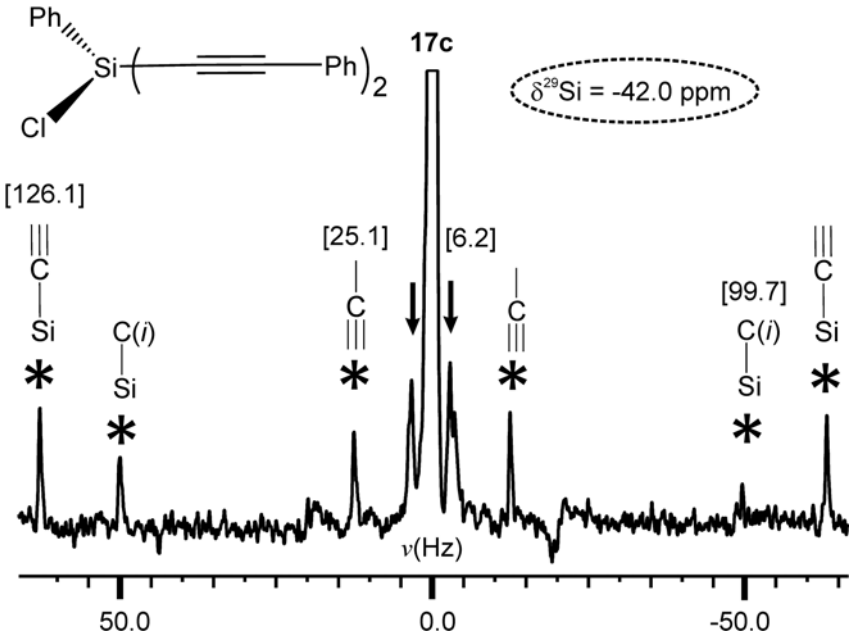


Figure 2.4. 59.6 MHz $^{29}Si\{^1H\}$ NMR spectra of the Chloro(phenyl)diphenylethynyl-silane **17c** in C_6D_6 (15 %, v/v). Only expansion is shown for the signal, ^{13}C satellites correspond to coupling constants $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$ are marked by asterisks. Further satellites are visible close to the parent signal, which may be assigned to $J(^{13}C,^{29}Si)$ coupling over ≥ 2 bonds.

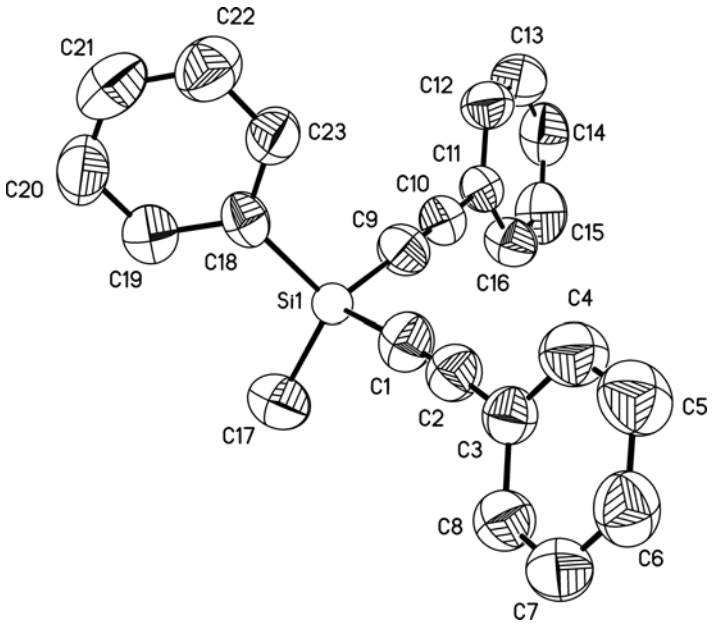
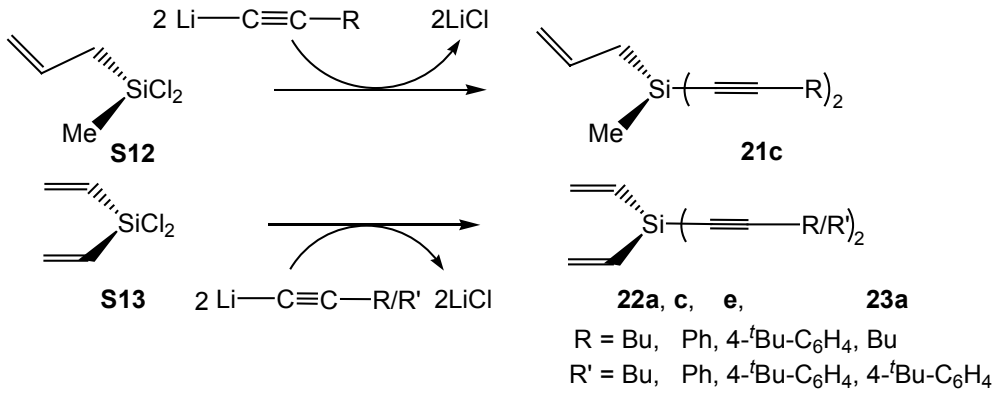


Figure 2.5. Molecular structure of silane **13c** (ORTEP plot, ellipsoids drawn at 50% probability level, hydrogen atoms are omitted for clarity). Selected bond lengths (pm) and angles (deg.): Si1-C1 181.4 (4), Si1-C17 183.6 (4), Si1-C18 185.1 (4), C1-C2 120.7 (5), C2-C3 142.9 (5), C1-Si1-C9 107.8 (16), C1-Si1-C17 109.6 (19), C1-Si1-C18 107.7 (18), C17-Si1-C18 112.0 (18), C9-Si1-C18 110.1 (17), C2-C1-Si1 175.6 (3), C1-C2-C3 176.8 (4), C4-C3-C2 121.6 (4).

2.4. Dialkyn-1-ylsilanes bearing Si-vinyl, Si-allyl and Si-divinyl functions

The dialkyn-1-yl(vinyl)silanes **19** and **20** were achieved as side products in the mixtures of silanes **8** and **9** (Scheme 2.4). The lighter fractions bearing one alkyn-1-yl group (**8** and **9**) were separated by fractional distillation. The silanes **19** and **20** were left in fairly pure form (ca. 90 %, overall yield 30 - 35 %), see Figure 2.6 (left trace) for ^{29}Si NMR spectrum of **19c**. Such silanes are attractive starting materials for heterocyclic systems *e.g.,* 1-silacyclopent-2-enes and were used in further chemical processes.

The choice of functional groups was extended and allyl(diphenylethynyl)silane (**21c**) and dialkyn-1-yl(divinyl)silanes (**22**, **23**) were considered in the next series. These silanes were prepared by the reaction of two equivalents of alkynyl lithium and one equivalent of allyl(dichloro)silane or dichloro(divinyl)silanes, respectively (Scheme 2.6). Reactions were carried out at 0 °C and sufficiently high yield (95 - 98 %) was obtained. All volatile materials and lighter fractions were removed at high temperature (80-100 °C) and reduced pressure. Pure samples obtained were fully characterized by multinuclear NMR spectroscopy (Figure 2.6).



Scheme 2.6. Twofold Cl-substitution of allyl(dichloro)silanes and dichloro(divinyl)-silanes to afford dialkyn-1-yl(allyl)silane **21c** and dialkyn-1-yl(divinyl)silanes **22a - e**, **23a** respectively.

NMR spectroscopy

The ^{13}C, ^{29}Si and ^{1}H NMR data of the dialkyn-1-yl(divinyl)silanes **22** and **23** are given in Table 2.8 and Experimental part, respectively. All ^{13}C NMR signals are within the expected range. The satellites owing to $J(^{13}C,^{29}Si)$ spin-spin coupling are helpful in the structural assignments. Different carbon atoms can be distinguished from each other either by coupling constants or by their characteristic frequency ranges. The ^{29}Si NMR signals were observed in the range of -46.2 ppm (**19c**) and -51.8 ppm (**20a**), close to the chemical shift of silane **18c** (-49.2 ppm). This comparison proved once again that the effect of Si-Ph group is almost similar to Si-vinyl group, on silicon chemical shift.

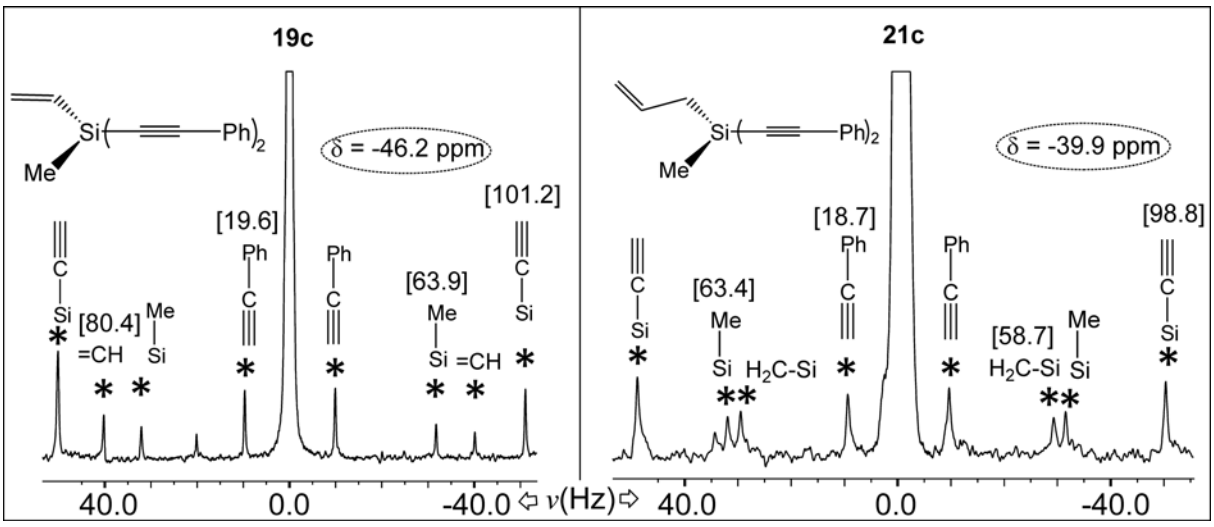
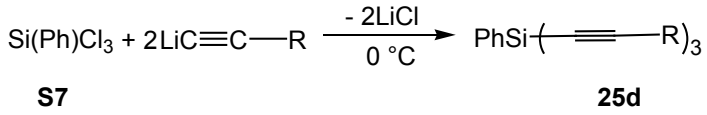


Figure 2.6. $^{29}Si\{^{1}H\}$ NMR spectra (59.57 MHz) of **19c** (left) and **21c** (right) satellites marked by asterisks corresponding to $J(^{13}C,^{29}Si)$ spin-spin coupling constants.

2.5. Trialkyn-1-ylsilanes

The silanes of general formula $R^1Si(C{\equiv}C\text{-}R)_3$ were obtained from reaction mixtures along with the monoalkyn-1-ylsilanes **5**, **6** and dialkyn-1-ylsilanes **16**, **17** (Scheme 2.2), or they were prepared by the reaction of one equivalent of alkyl(trichloro)silanes with three equivalents of alkynyl lithium (Scheme 2.7). The latter is a more convenient method of the preparation because the yield can be increased to 95 %. The stated silanes were isolated from the mother solution as solid crystalline materials (**24c**, **25c** and **25d**), or as an oily liquid (**24a**) by fractional distillation.



Scheme 2.7. Synthesis of tri(*p*-tolylethynyl)phenylsilane **25d**.

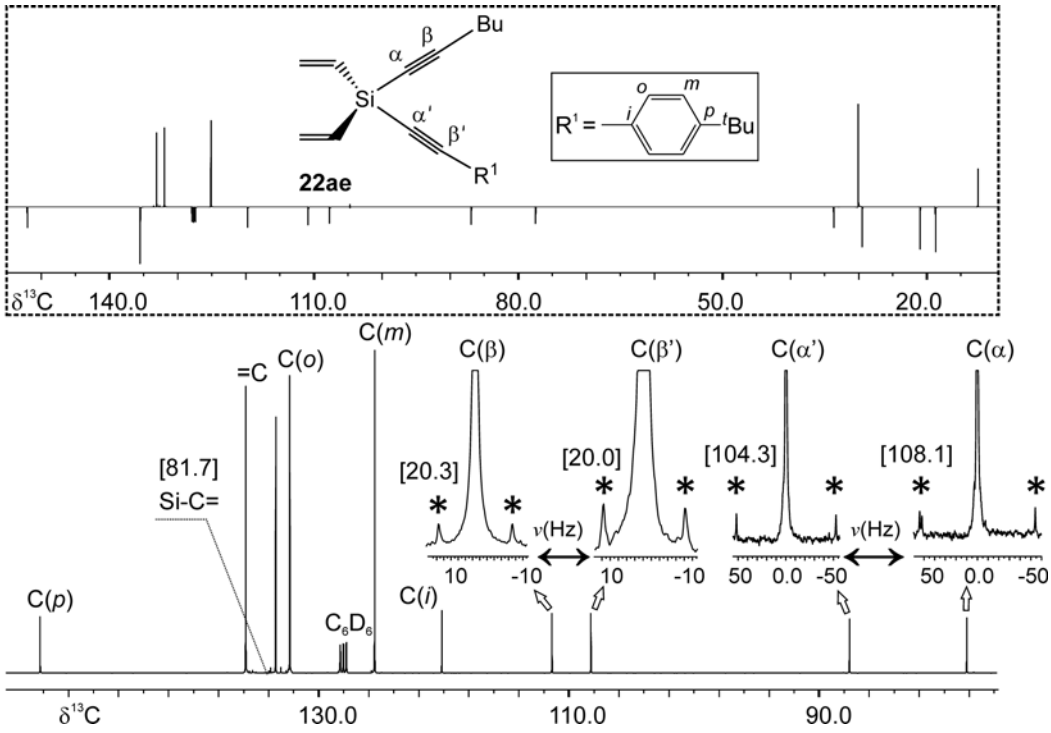


Figure 2.7. 100.4 MHz $^{13}C\{1H\}$ NMR spectra (lower trace), of dialkyn-1-yl(divinyl)silane **23a**, where two different organyl groups are present at Si-C≡C- atom. The R and R' groups are well distinguished from their characteristic ^{13}C chemical shifts and coupling constants. Expansions are given for Si-C≡C- atoms, with $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$ coupling. The full J-modulated spectrum (upper trace) is given where all carbons can be assigned unambiguously.

NMR spectroscopy

The NMR data (^{13}C, ^{29}Si) related to silanes **24** and **25** are summarized in Table 2.9 and ^{1}H NMR data in Experimental part. The ^{13}C NMR data (Si-C≡C-) covers a narrow range of 108 to 110 ppm for β–carbon atoms and relatively wider range of 78 to 89 ppm for α-carbon atoms. The $\delta^{13}C$ data of -C≡C- carbons as well as for the other carbon atoms belonging to 'R' groups are in the expected range. The coupling constants $^{1}J(^{13}C,^{29}Si)$ and $^{2}J(^{13}C,^{29}Si)$ are larger than for dialkyn-1-ylsilanes **11-14** (Table 2.9 and Table 2.4 for comparison). The ^{29}Si-NMR spectra of **24** and **25** exhibit the silicon resonance signals at relatively high field, –63.5 (**21c**) to -71.9 ppm (**22a**), in support of the suggested structures. The ^{29}Si NMR spectra were recorded for sufficiently long time (for few compounds) and suitable signal-to-noise ratio was achieved in order to confirm all the $J(^{13}C,^{29}Si)$ coupling constants measured from ^{13}C NMR spectra (Figure 1.1D and Figure 2.8). The ^{1}H-NMR data (given in Experimental part) of the title silanes are also consistent with the proposed structures.

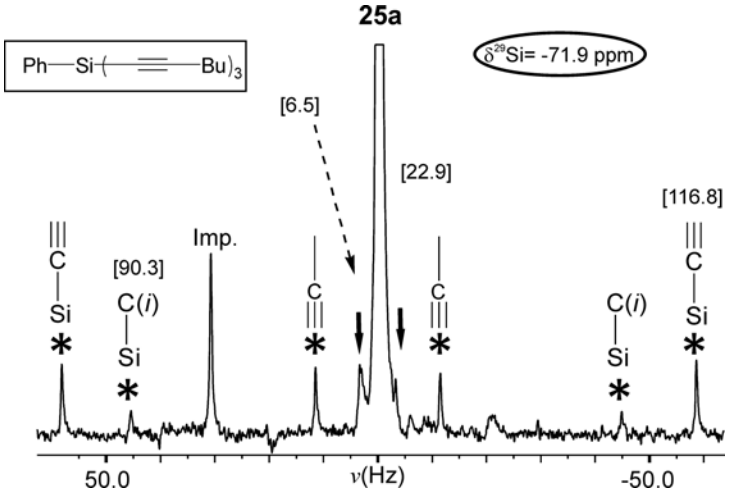


Figure 2.8. 59.6 MHz $^{29}Si\{^{1}H\}$ NMR spectra of the tri(hex-1-yl)phenylsilane **25a**. Expansion of the parent signal is given, ^{13}C satellites marked by asterisks, correspond to coupling constants $^{1}J(^{13}C,^{29}Si)$ and $^{2}J(^{13}C,^{29}Si)$. Further satellites close to parent signal are visible, due to $^{n}J(^{13}C,^{29}Si)$ (n ≥ 2).

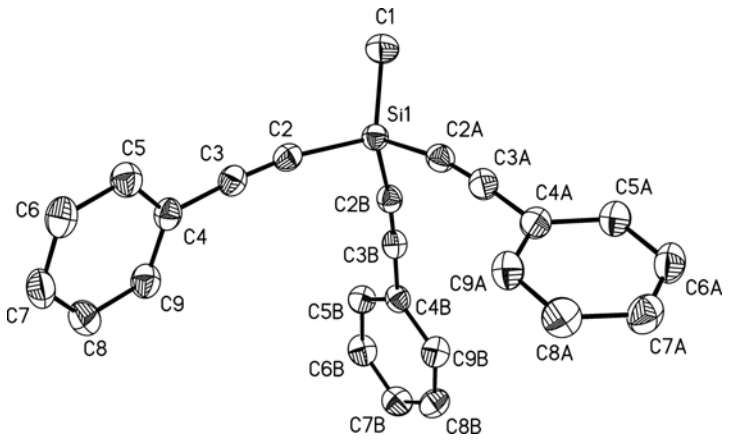


Figure 2.9. Molecular structure of tri(phenylethynyl)methylsilane **24c**, (ORTEP plots, ellipsoids drawn at 30 % probability level, hydrogen atoms are omitted for clarity). Selected bond lengths (pm) and angles (deg.): C1-Si1 182.5 (3), C2-C3 120.4 (2), C2-Si1 182.1 (17), C3-C4 143.4 (2), C4-C5 139.9 (2), C2-C3-C4 175.5 (19), C9-C4-C5 119.5 (16), C5-C4-C3 120.4 (16), C2-Si1-C2 106.0 (6), C2-Si1-C1, 112.8 (5), C3-C2-Si1 169.8 (15).

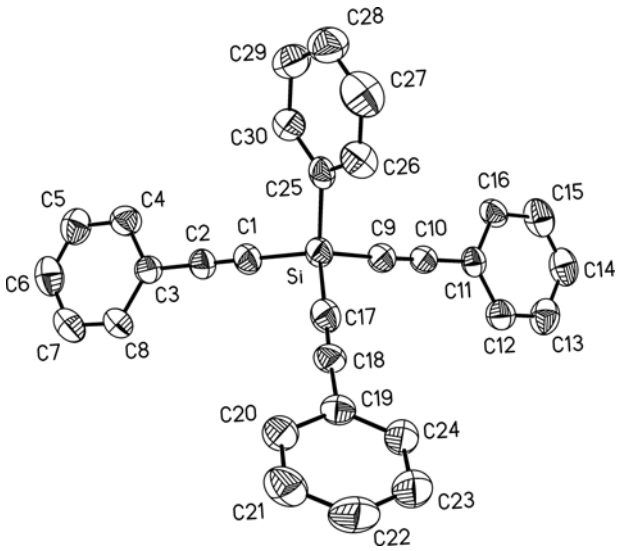


Figure 2.10. Molecular structure of tri(phenylethynyl)phenylsilane, **25c** (ORTEP plots, 30 % probability level, hydrogen atoms are omitted for clarity). Selected bond lengths (pm) and angles (deg): Si-C25 186.5 (7), C1-C2 119.9 (9), Si-C1 182.9 (8), C2-C3 144.1 (10), C3-C4 140.4 (10), C1-C2-C3 177.2 (7), C4-C3-C8 119.1 (7), C4-C3-C2 119.3 (6), C9-Si-C1 109.7 (3), C1-Si-C25 109.0 (3), C2-C1-Si 179.3 (7).

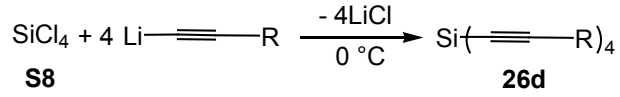
*X-Ray structural analyses of trialkyn-1-ylsilane **24c** and **25c***

The molecular structures of **24c** and **25c** are given in Figure 2.9 and Figure 2.10 respectively together with selected bond lengths and angles. The data relevant to

crystal structure determination are given in Table 2.10. Although the crystal quality of **25c** was not good enough due to disordered toluene molecules used as the solvent for crystallization, but the bond lengths and angles are comparable with the analogous structure **24c**. The surrounding of silicon atom in **24c** is distorted tetrahedral and in **25c** it is tetrahedral (all angles in the range of 109 - 110°). All other bond lengths and angles are within the expected range. In the molecule of **24c** all the three angles ∠ C2-Si1-C2 = 106° are contracted as compared to ∠ C2-Si1-C1 = 112.8°. The intermolecular or intramolecular short contacts were negligible.

2.6. Tetraalkyn-1-ylsilanes

So far the silanes bearing one, two and three Si-C≡C-R groups are discussed. The next challenge was to isolate tetraalkyn-1-ylsilanes in pure form and to use them for the synthesis of some heterocycles (spirosilanes, *vide infra*). These silanes were prepared by treating tetrachlorosilane with four equivalents of freshly prepared alkynyl lithium, as represented in Scheme 2.3, or they were synthesized in relatively high purity (> 90 %) as shown in Scheme 2.8. All the members of the series were solid crystalline materials, a characteristic that was particularly important in getting of these silanes in pure forms.



Scheme 2.8. Reaction of one equivalent of tetrachlorosilane with four equivalents of alkynyl lithium to afford tetraalkyn-1-ylsilane derivative **26d**.

NMR spectroscopic studies

Although tetraalkyn-1-ylsilanes **26b** and **26c** have been studied earlier but the important data are recollected along with some missing information such as, $J(^{13}C,^{29}Si)$ coupling constants. The study of the silanes discussed so far reveals a gradual increase in the value of coupling constants with the increase in the number of alkyn-1-yl functions. The role of chlorine atom in increasing the value of coupling constants is more prominent if compared with alkynyl groups. The ^{13}C NMR data of the title silanes are in expected range.[42,91,92] The ^{29}Si NMR signals shift to highfield (> -90 ppm), which is the characteristic range for four alkyn-1-yl groups linked to

silicon. The structural elucidations are strongly supported by coupling constants and ^{29}Si chemical shifts.

*X-ray structural analysis of tetra(p-tolylethynyl)silane **26d***

The molecular structure of **26d** is shown in Figure 2.11 together with the bond lengths and angles. The other related information are given in Table 2.12. The unit cell contains eight molecules which is smaller than the analogous silane $Si(C{\equiv}C\text{-}Me)_4$ (sixteen molecules per unit cell)[92] and larger than the two other similar silanes $Si(C{\equiv}C\text{-}SiMe_3)_4$[93] and $Si(C{\equiv}C\text{-}^tBu)_4$[94] (four molecules each, per unit cell). The geometry around silicon atom slightly deviates from the perfect tetrahedral.

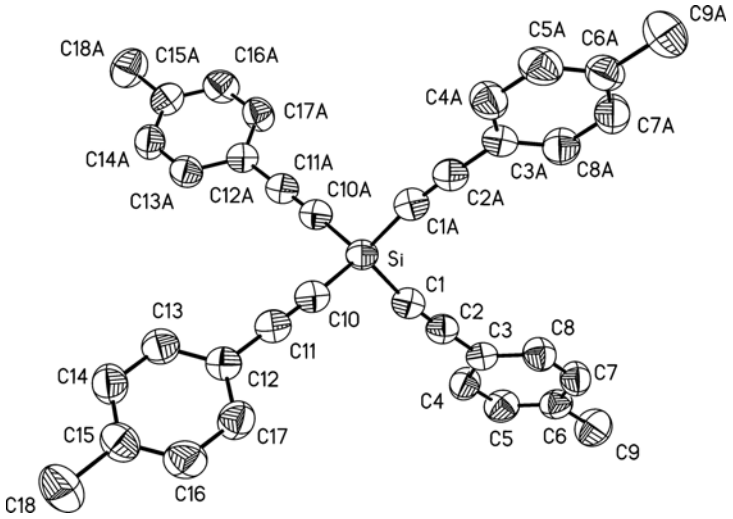


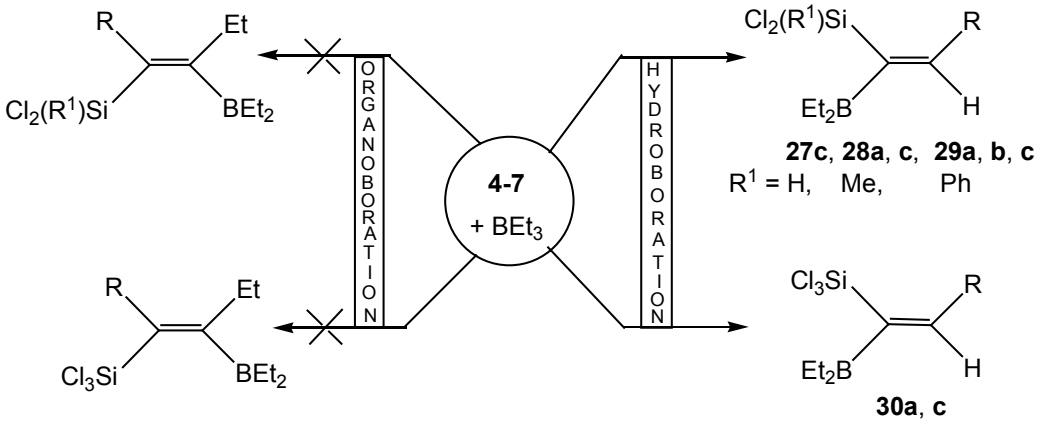
Figure 2.11. Molecular structure of tetra(*p*-tolylethynyl) silane **26d**. (ORTEP plot drawn at 40 % probability level, hydrogen atoms are omitted for clarity). Selected bond lengths (pm) and angles (deg): Si-C1 181.5 (2), C1-C2 120.3 (3), C2-C3 143.2 (3), C3-C4 138.9 (3), C3-C8 138.6 (3), C1-Si-C10 110.8 (9), C2-C1-Si 172.4 (19), C1-C2-C3 177.7 (2), C4-C3-C8 117.8 (2).

3. 1,2-HYDROBORATION

3.1. 1,2-Hydroboration of monoalkyn-1-ylsilanes

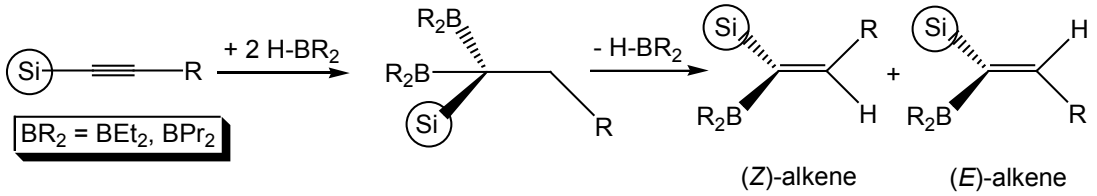
3.1.1. BEt_3 as hydroborating reagent

It has been stated that the B-C bond in BEt_3 is very stable and does not undergo cleavage,[95] and in the gas phase ethene elimination is extremely slow (Scheme 3.4) if compared with olefin elimination (1-butene, 1-pentene, 2-pentene, 1-hexene, 1-propene etc.) from other trialkylboranes. At high temperature (109 - 214 °C) it does not react with acetylene.[96] Triethylborane has been used in many reactions where it acts as organoborating reagent.[29,51d,85] Up till now no reactions have been outlined where it acts as hydroborating reagent. Since the main emphasis in this work was the presence of functional groups such as Si-H and Si-Cl in addition to the alkynyl group, alkyn-1-ylsilanes bearing Cl_2Si- and Cl_3Si- moieties were considered and treated with excess of BEt_3. This served as a reagent as well as the solvent under the reported harsh reaction conditions. Surprisingly, the reactions followed a completely different route and 1,2-hydroboration was observed (Scheme 3.1) instead of 1,1-organoboration. The reactions were carried out at elevated temperatures (110 - 120 °C) for several days in sealed NMR tubes or pressure safe closed Schlenk tubes (Experimental part). The products were identified by their characteristic NMR data. The data pattern revealed that silicon and boron atoms are linked to the same olefinic carbon atom.



Scheme 3.1. Two possible path ways for BEt_3 to react with alkyn-1-ylsilanes. The 1,1-ethylboration and 1,2-hydroboration, here 1,2-hydroboration is the favourable route.

The product contains (*Z*)-alkenes together with a small amount of (*E*)-alkenes, can be identified from their characteristic NMR data (^{1}H, ^{13}C and ^{29}Si). The formation of these isomers and loss in selectivity may be explained on the basis of twofold hydroboration caused by 'H-BEt_2' species produced *in situ*. In next step the dehydroboration affords (*Z*)-alkenes as the principle product together with small amount of (*E*)-alkenes (Scheme 3.2).



Scheme 3.2. Reasons for loss of selectivity, where twofold hydroboration is the proposed key factor. The encircled silicon bears either -SiR^1Cl_2 surroundings or -$SiCl_3$.

NMR spectroscopy

The data set of ^{1}H, ^{11}B, ^{13}C and ^{29}Si NMR for alkenylsilanes **27 - 30** is summarized in Experimental section and Table 3.1. The formation of the products as a result of 1,2-hydroboration can be confirmed by ^{13}C NMR data of BEt_2 group, in aliphatic region where no ^{13}C NMR signals for Et group were observed (see Figure 3.1 for ^{13}C and ^{29}Si NMR spectra of **30c**). For olefinic carbons one broad (BC=)[98,97] and one sharp signal (=CH) without ^{29}Si coupling satellites leave no doubt about the proposed (1,2-hydroboration) reaction and the substituent pattern. The formation of (*E*)-isomers can be seen from the observation of another set of NMR signals in ^{13}C and ^{29}Si spectra.

In the ^{1}H NMR spectrum, the signal belong to =CH, in olefinic region 6 - 7 ppm, with satellites for $^{3}J(^{1}H,^{29}Si) \approx 35$ Hz strongly support the proposed structure and nature of the reaction.

3.1.2. BPr_3 as hydroborating reagent

In connection with previous results obtained concerning BEt_3, it seemed of interest to study the reaction behaviour of BPr_3 with the same silanes **5 - 7**. It has already been reported that BPr_3 can act as hydroborating reagent with some nitrogen-containing compounds[99] and 2-pentene, etc. to afford a mixture of pentylboranes at elevated temperature (160 - 300 °C).[100] The reactions of BPr_3 with

alkyn-1-ylsilanes where it acts as hydroborating reagent have not been reported. However, on the basis of previous findings[99,100] one expects 1,2-hydroboration by treating BPr_3 with alkyn-1-ylsilanes **5 - 7**.

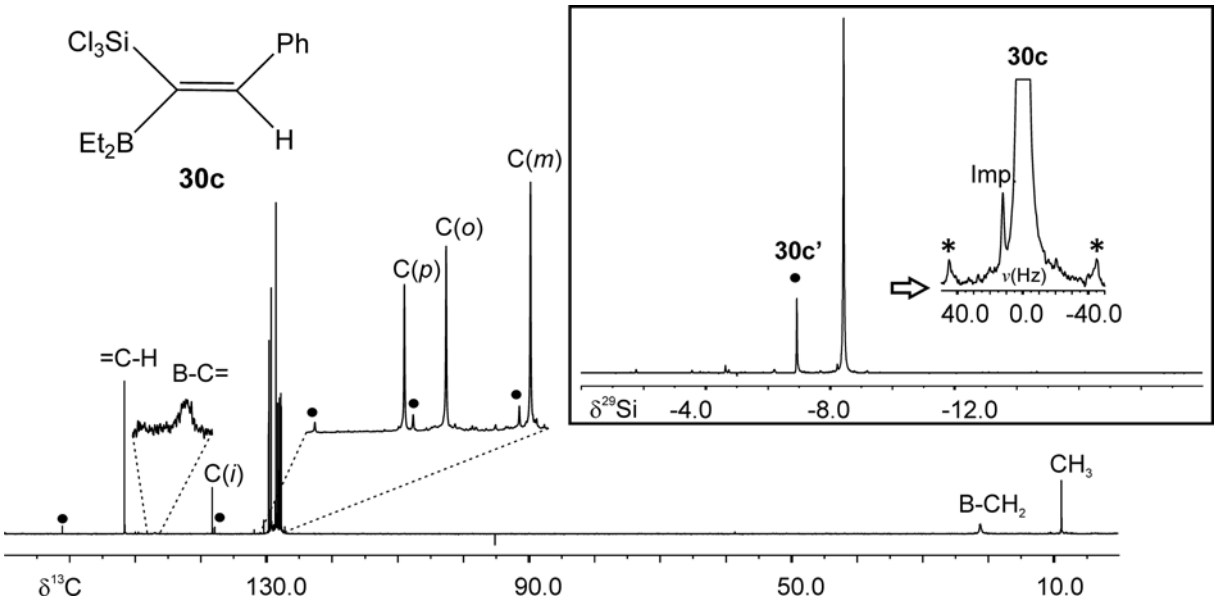
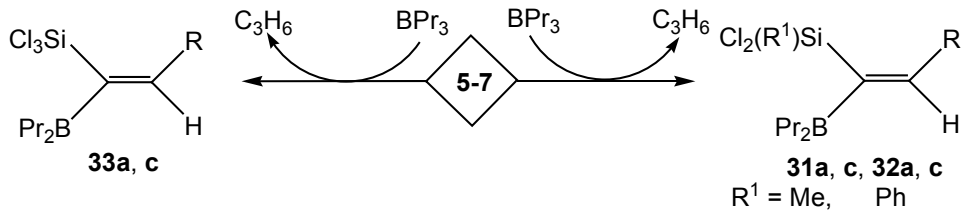


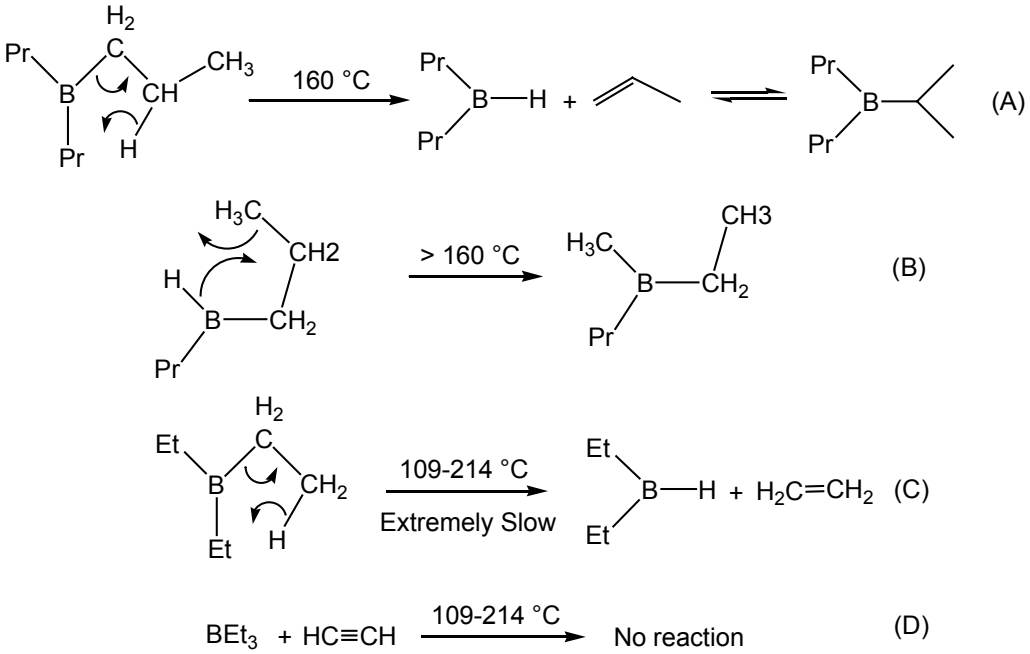
Figure 3.1. 100.5 MHz $^{13}C\{^1H\}$ and 59.6 MHz $^{29}Si\{^1H\}$ (inserted) NMR spectra of alkenylsilane **30c**, the second isomer **30c´** (marked by black circles) is evident from weak additional signals in both the spectra. Expansion is shown for ^{29}Si NMR signal (major product) with ^{13}C satellites correspond to $^1J(^{13}C,^{29}Si)$.



Scheme 3.3. 1,2-hydroboration observed for BPr_3 when treated with alkyn-1-yl(dichloro)- and alkyn-1-yl(trichloro)silanes.

These reactions remind of the findings of R. Köster *et al.,*[101] where pyrolysis of tripropylboranes at high temperature (≈ 300 °C) generates Pr_2B-H, followed by formation of unsymmetrical triorganoboranes (Scheme 3.4). The Pr_2B-H undergoes various rearrangements in the absence of a suitable scavenger, *i. e.* silane bearing Si-C≡C- unit used in this work. The same specie Pr_2B-H is proposed to be generated '*in situ*' in reactions of BPr_3 with alkyn-1-yl(chloro)silanes at relatively low temperature 100 - 120 °C. It shows that the Si-Cl function stabilizes the Si-C≡ bond. The cleavage

of B-C(Pr) bond is favoured to give Pr_2B-H *via* 1,2-dehydroboration which reacts with the C≡C bond by 1,2-hydroboartion. Isomerisation was observed in reactions of BPr_3 with silanes **5 - 7**. It can be explained in the same way that twofold hydroboration of alkyn-1-ylsilanes takes place, followed by dehydroboration and isomers with *E* and *Z* configuration can be detected.



Scheme 3.4. Formation of Pr_2BH during pyrolysis of BPr_3. BEt_3 does not afford Et_2BH even in presence of acetylene.

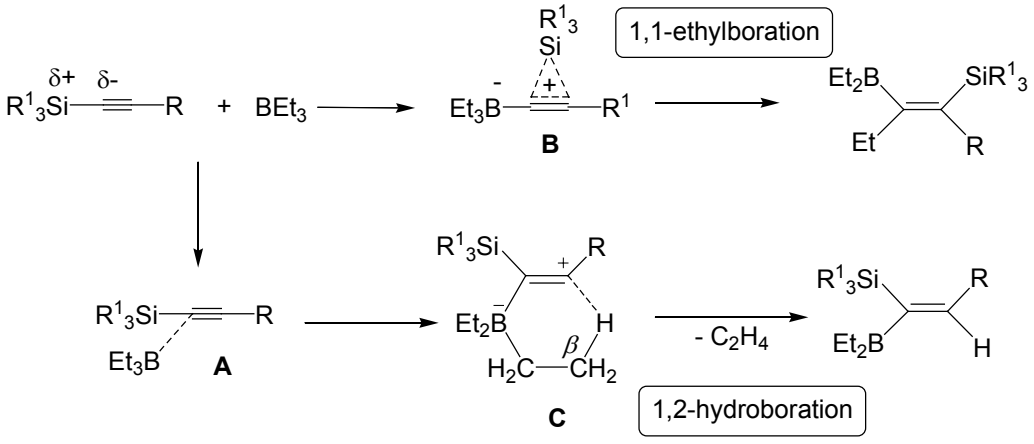
NMR spectroscopy

The NMR spectroscopic data (^{11}B, ^{13}C, ^{29}Si and ^{1}H) for dipropylboryl-substituted alkenylsilanes **31 - 33** are listed in Table 3.2 and Experimental section. The reactivity of tripropylborane, BPr_3, was found to be similar to that of BEt_3. The NMR data correspond to those obtained for diethylboryl-substituted alkenylsilanes **27 - 30** and support the proposed structures (Scheme 3.2). These results have been discussed in two of our research paper.[102]

Proposed Reaction mechanism

There is no doubt in the case of BPr_3 that it slowly decomposes upon heating > 80 °C *via* 1,2-dehydroboration into propene and Pr_2BH which then reacts with alkynes or alkenes in the usual way as a 1,2-hydroborating reagent.[103] In contrast, even under much more harsh conditions, BEt_3, does not undergo elimination of

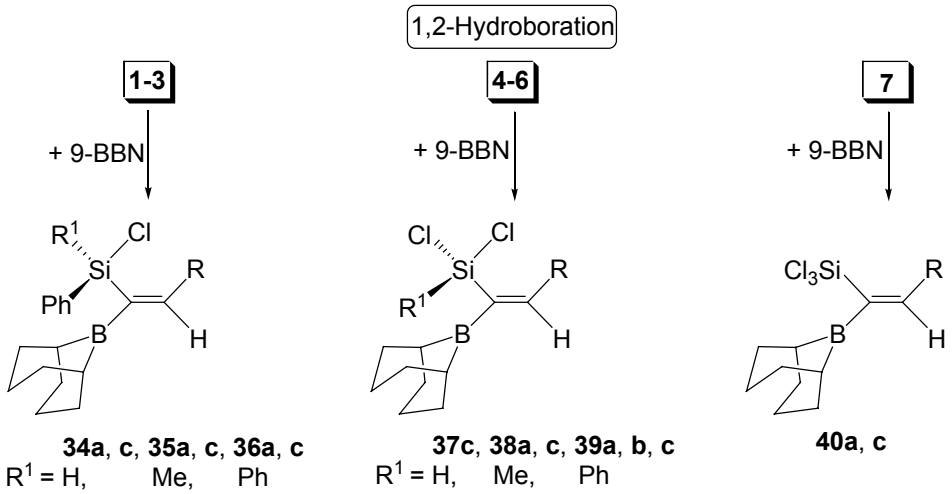
ethene to give dialkylboron hydrides Et_2BH. Nevertheless, BEt_3 acts as hydroborating reagents in the presence of certain alkyn-1-ylsilanes. An explanation is offered in Scheme 3.5, where the first interaction **A** between the borane and the alkyn-1-ylsilane is the same for 1,1-ethylboration and 1,2-hydroboration. Cleavage of the Si-C≡ bond leads to a borate-like zwitterionic intermediate **B**[29] and finally to 1,1-ethylboration.[29,85] If the Si-C≡ bond is strong, cleavage of this bond does not occur, leaving alternative routes. In particular for substituents R^1 capable of delocalizing a positive charge (*e.g.,* R^1 = Ph), an intermediate **C** will be stabilized and transfer of a hydrogen atom from the β-carbon atom is favoured to give the 1,2-hydroboration product accompanied by elimination of ethene. Compelling evidence for the influence of R^1 is provided by comparison of the reaction of $Cl_2(H)Si\text{-}C{\equiv}C\text{-}Bu$[85] (1,1-ethylboration) and $Cl_3Si\text{-}C{\equiv}C\text{-}Bu$ with BEt_3[102a] (Scheme 3.1; 1,2-hydroboration). The β-hydrogen transfer in Scheme 3.5 reminds of one of the processes proposed for limiting the chain lengths of polymers and it has been discussed in the chemistry of aluminum alkyls.[104] It may also be important in the catalyzed high-temperature alkane isomerisationof alkanes caused by carbenium ions[105] which are isoelectronic with boranes. The reactions were carried out for a number of alkyn-1-ylsilanes and from a series of compounds it was concluded that the BEt_3 can also act as hydroborating reagent. This is of considerable importance since BEt_3 is a commercial compound. Otherwise 'BEt_2H' has to be generated from the reaction of BEt_3 and diborane(6) which lead to a mixture containing $Et_2BH_2BEt_2$, $Et_2BH_2B(H)Et$ and BEt_3 in various concentrations.[106]



Scheme 3.5. Proposed mechanism for the reactivity of BEt_3 as a hydroborating reagent towards certain alkyn-1-ylsilanes in competition with 1,1-ethylboration.

3.1.3. 9-BBN as hydroborating reagent

The 1,2-hydroboration reactions of alkyn-1-yl(chloro)silanes using 9-BBN have been reported.[45] The 1,2-hydroboration of the alkyn-1-ylsilanes is straightforward in most cases, and the resulting alkenes have already been used for further reactions.[49,50,73,75] During performing this work, the well known hydroborating reagent, 9-BBN, was used for 1,2-hydroboration of alkyn-1-ylsilanes bearing up to three Si-Cl functions as shown in Scheme 3.6. The previously reported results were expected. The substituents pattern of 1,2-hydroboration products is evident from a consistent set of NMR spectroscopic data (Table 3.3, Table 3.4 and Experimental Section). These reactions were carried out with the hope to get single crystals (if possible) suitable for X-ray diffraction and to study their role in further reactions. The Si-Cl function reduces the reactivity of the C≡C bond towards 1,2-hydroboration. Therefore, the reactions were performed at elevated temperature (80 - 100 °C). Almost all products were oily liquids and few were crystalline materials. They were used in further reactions without purification.

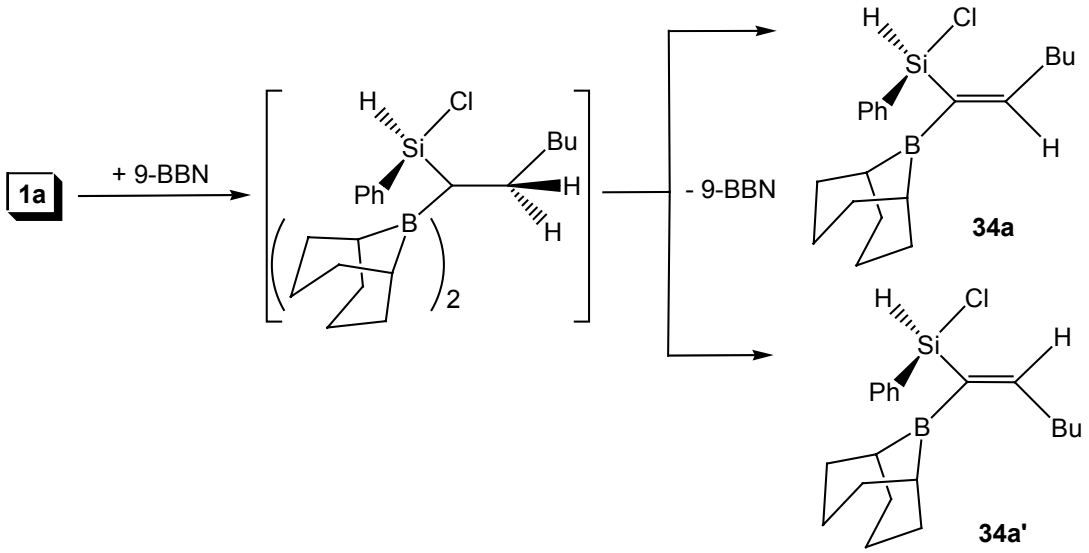


Scheme 3.6. Syntheses of boryl-substituted alkenylsilanes.

The reactions proceed *via* a four-membered short lived C-B-C-H intermediate as shown in Scheme 1.2. The progress of the reactions was monitored by ^{29}Si NMR spectra measured directly for the reaction solutions. The solution state NMR data of all the reactions support the proposed structures (**34 - 36**), except in the case of silane **34a** with 9-BBN, where the selectivity was lost. The reaction was carried out at room temperature in THF as well as at 80 °C in toluene as solvents. The reaction afforded a mixture of isomers **34a** and **34a´**, independent of the reaction conditions.

These results can be explained considering a fast second hydroboration of the alkene **34a** leading to 1,1-diboryl-1-silylhexane (not detected) as intermediate (Scheme 3.7). Upon dehydroboration they afford mainly the mixture of (*Z)*isomer together with small amount of (*E)*isomers **34a** and **34a´**, respectively. The presence of both alkenes in the mixture is shown by a set of NMR signals (Table 3.3 and Experimental Section).

The characteristic features of 1,2-hydroboration are high regioselectivity, clean formation of alkenes and excellent yield, for example (see Figure 3.3, showing the ^{13}C NMR spectra of the unpurified alkene **39a**). Another positive aspect is, a variety of organic and inorganic functional groups can be easily included on the silicon atom as well as on Si-C≡C- unit. Silanes bearing up to three Si-Cl function(s) and Si-C≡C-R (R = Bu, ^{t}Bu and Ph) in addition to the alkenyl function were prepared. Pure samples of the silanes **4 - 7** were treated with 9-BBN, in the same way as discussed for alkenes **34 - 36**. All the reactions proceed smoothly towards the expected destination (alkenes **37 - 40**) and no side reactions were observed.



Scheme 3.7. Potential reasons for the loss of stereo- and regioselectivity of the 1,2-hydroboration of chloro(hexyn-1-yl)phenylsilane **1a**.

NMR spectroscopy

The stereochemistry proposed for the solution-state structure of the alkenes **34** - **40** is in agreement with the results of ^{1}H NMR spectroscopy using 1H/1H-NOE difference spectra.[108] The proton attached to olefinic carbon (-C=CH) atom appears in the aromatic region (6.9 - 8.2 ppm). This proton can be identified as a triplet for R =

Bu and a singlet for R = ^{t}Bu, Ph and *p*-tolyl. In the case of a singlet, ^{29}Si satellites can be observed, corresponding to $^{3}J(^{1}H,^{29}Si)$ coupling constants, ranging from 20 - 35 Hz. The pattern of substituents at the C=C bond can also be assigned unambiguously on the basis of the ^{13}C NMR data. An inspection of Table 3.3 and Table 3.4 clearly indicates that the alkenes possess analogous structures. In the olefinic range, the presence of a broad weak signal is typical for the carbon atom bonded to boron.[97,98] Since the sharp signal for =CH carbon atom does not show ^{29}Si satellites ($^{2}J(^{13}C,^{29}Si)$ < 3 Hz), it means the silyl group is attached to the same olefinic carbon atom to which the boryl group is linked. In principle, the coupling constant $^{1}J(^{13}C,^{29}Si)$ for (B)C= can hardly be observed in ^{13}C NMR spectra owing to broadness and very week intensity of this signal. It is difficult to obtain the signal-to-noise ratio required for obtaining such information. The most convenient access to these data $^{1}J(^{13}C,^{29}Si)$ is provided by observing the ^{13}C satellites in the ^{29}Si NMR spectra. This is shown in Figure 3.2 for three representative alkenes. The presence of the boryl group at the same olefinic carbon[107,109] typically reduces the magnitude of $^{1}J(^{13}C,^{29}Si)$ in the order of 10 to 15 Hz in comparison with other alkenylsilanes. The ^{11}B chemical shifts[108] are characteristic for alkenyl(dialkyl)boranes, in which a conformation is preferred where the boryl group is significantly twisted against the B–C=C plane. The ^{29}Si chemical shifts are in the expected range considering the various substituent effects.[107,109] For each conversion of -C≡C- into -C=C- the ^{29}Si NMR signal is shifted 15 - 20 ppm downfield (high frequency). Most of these results are summarized in two of our research articles.[111,112]

*X-ray structural analyses of compounds **35c**, **37c** and **39c***

Molecular structure of **35c**, **37c** and **39c** are shown in Figure 3.4, Figure 3.5, and Figure 3.6, respectively. Selected bond lengths and angles are listed in Table 3.6 and the data relevant to the crystal structure determination are given in Table 3.7. The geometry around boron atom is trigonal planar in all molecules, sum of CBC angles is 359.4° (**35c**), 360.0° (**37c**) and 359.4° (**39c**). The distances between chlorine atoms and the boron are long: 407.6 pm (**35c**), 354.3 pm, 397.0 pm (**37c**) and 459.1 pm, 409.1 pm (**39c**). Hence, no B-Cl-Si or B-H-Si bridgings can be proposed at least in the solid state. All other bond lengths and angles are well comparable with structural data already published for two analogous alkenylsilanes.[45] In the latter, it appears that the Si-Cl function prefers an orientation

towards the boryl group and one was tempted to propose a weak donor-acceptor interaction, a B-Cl-Si bridge, in the solid state. In solution, however, the NMR data for compounds of such type indicate the absence of these interactions. In compounds **35c**, **37c** and **39c** the Si(B)C=C atoms are in the same plane. This plane is regarded as the reference plane.

In the molecule of **35c** CBC (9-BBN) and Ph (C11 - C16) planes are twisted against the reference plane by 134.8° and 136.9°, respectively. The CBC plane of 9-BBN in **37c** is twisted by 37° and Ph plane (C11 - C16) by 41.9° against the reference plane. The CBC plane of the 9-BBN group in **39c** is oriented in such a way that it makes an angle of 18.3° with the reference plane. While the C-Ph and Si-Ph rings are twisted by 33.1° and 64.6°, respectively.

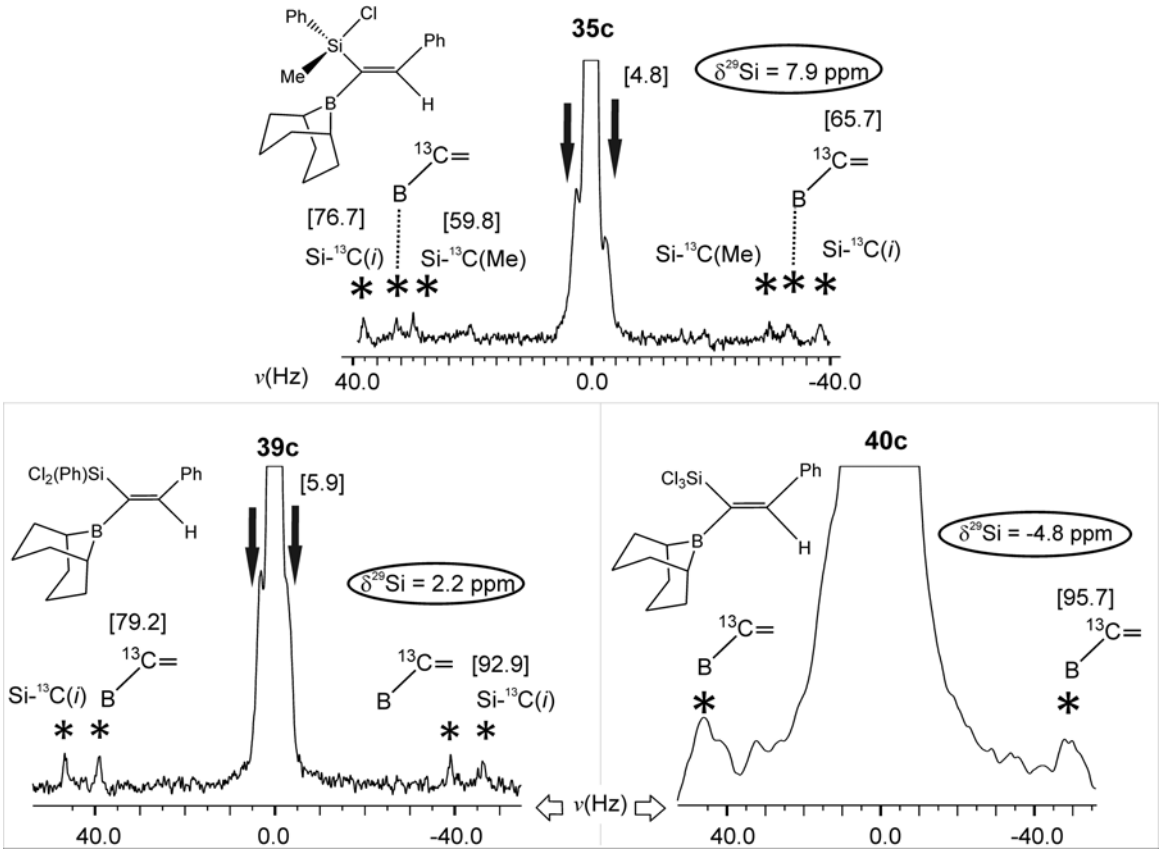


Figure 3.2. 59.6 MHz (upper), 99.4 MHz (lower left) and 79.47 MHz (lower right) $^{29}Si\{^{1}H\}$ NMR spectra of the alkenyl(chloro)silanes **35c**, **39c** and **40c**, respectively. The line widths of the ^{29}Si NMR signals increase with the number of chlorine atoms linked to silicon owing to unresolved scalar one-bond $^{35/37}Cl$-^{29}Si spin-spin coupling[107] and there is also a contribution from unresolved scalar two-bond coupling $^{2}J(^{11}B,^{29}Si)$. In **35c** and **39c**, further ^{13}C satellites are visible, close to the parent signal, arise from $^{n}J(^{13}C,^{29}Si)$ $n \geq 2$.

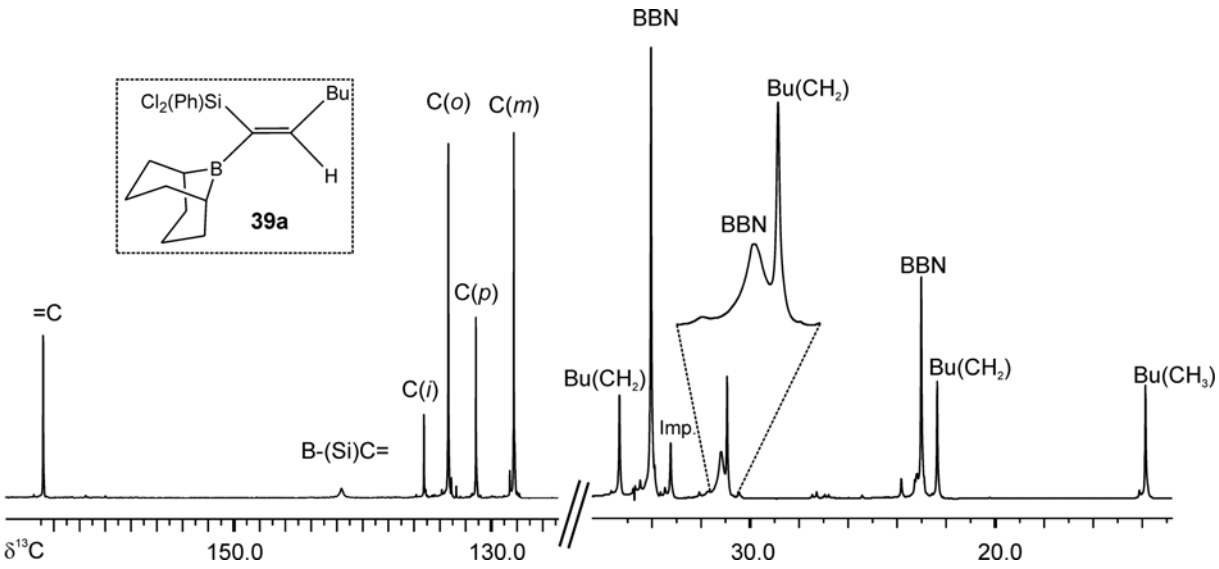


Figure 3.3. 75.4 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 9-[(dichlorophenylsilyl)-2-butyl-vinyl]-9-borabicyclo[3.3.1]nonane **39a**, with full assignment.

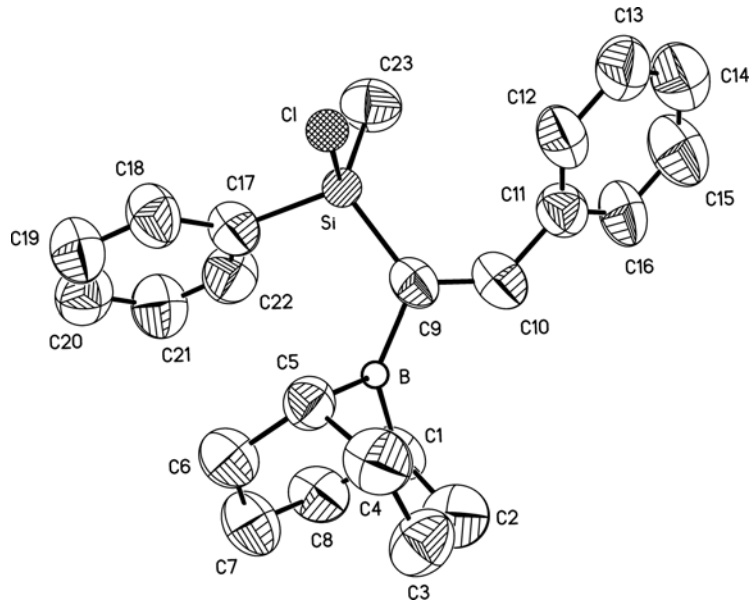


Figure 3.4. View of the molecular structure of alkenylsilane **35c** (ORTEP plot, 40 % probability level; hydrogen atoms are omitted for clarity) see Table 3.6 and Table 3.7 for selected structural parameters.

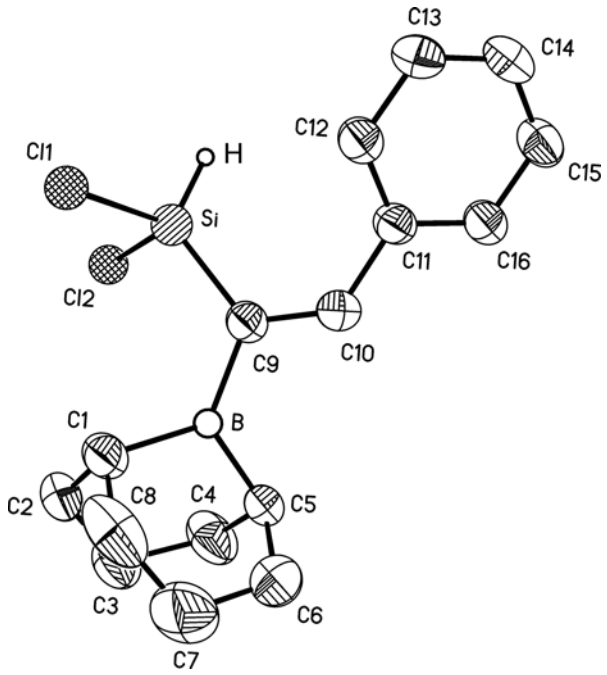


Figure 3.5. Molecular structure of boryl-substituted alkenylsilane **37c**, ORTEP plot drawn at 40 % probability level; all hydrogen atoms are omitted for clarity except Si-H) see Table 3.6 for selected bond lengths and angles.

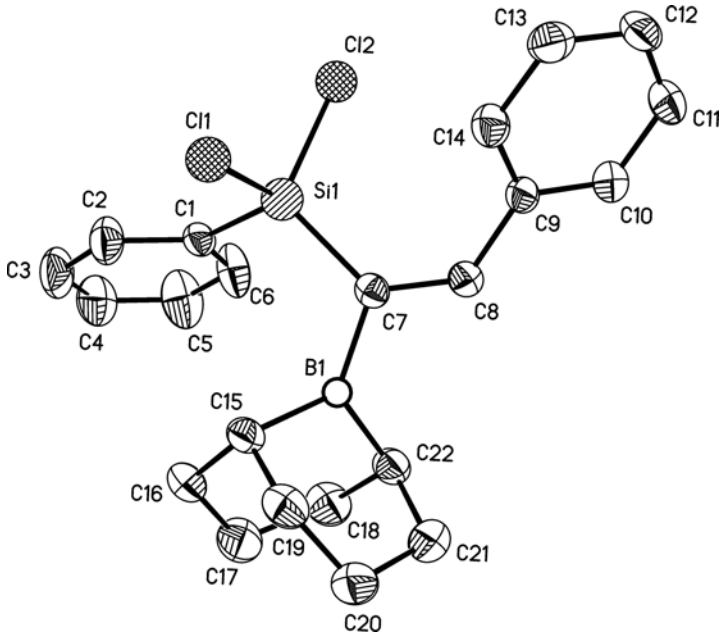
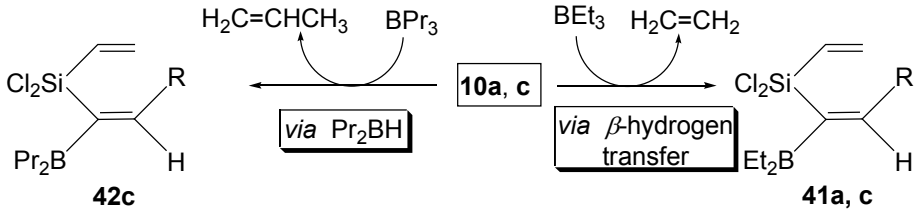


Figure 3.6. Molecular structure of boryl-substituted alkenylsilane **39c** (ORTEP plot drawn at 40 % probability; hydrogen atoms are omitted for clarity) selected structural parameters and listed in Table 3.6 and Table 3.7.

3.2. 1,2-Hydroboration of monoalkyn-1-yl(vinyl)silanes

3.2.1. Using BEt_3 as hydroborating reagent

Having established the potential activity of BEt_3 as hydroborating reagent, it was of some interest to know whether a Si-vinyl or Si-alkynyl group is preferred to be attacked by BEt_3, if it really generates "Et_2B-H" *in situ*. Therefore, the reaction of alkyn-1-yl(dichloro)(vinyl)silane **10** was studied. The results (Scheme 3.8) were similar to Brown's findings that the -C≡C- is more reactive than the -C=C bond towards hydroboration. This is even true for sterically hindered dialkylboranes such as dicyclohexylborane and disiamylborane.[113] In the reaction of alkyn-1-yl(dichloro)(vinyl)silane **10** with BEt_3 it was observed that the reaction takes place at Si-C≡C- bond leaving the Si-C=C function untouched.



Scheme 3.8. 1,2-Hydroboration of silanes **10a**, **c** using BEt_3 and BPr_3 as hydroborating reagent.

NMR spectroscopy

The NMR data of alkenyl(vinyl)silanes **41a** and **41c** are collected in Table 3.8 and Experimental section. The data pattern is in agreement with the previously discussed alkenylsilanes **27 - 40**. In both ^{13}C and ^{1}H NMR spectra, the resonance signals belonging to the vinyl group (see footnote of Table 3.8 and Experimental section) are very clear and can be assigned without any difficulty. It proves that the vinyl group is untouched and reactions occurred on Si-C≡C- bond affording the silanes **41a** and **41c**.

3.2.2. Using BPr_3 as hydroborating reagent

In a similar way tripropylborane (BPr_3) and alkyn-1-yl(dichloro)(vinyl)silane **10c** when react together, the vinyl group is left untouched, and the formation of alkenylsilane (**42c**) was observed. The reaction was fast in contrast to that of BEt_3.

The aim of this reaction was to support the information obtained for silane **41a** and **41c**.

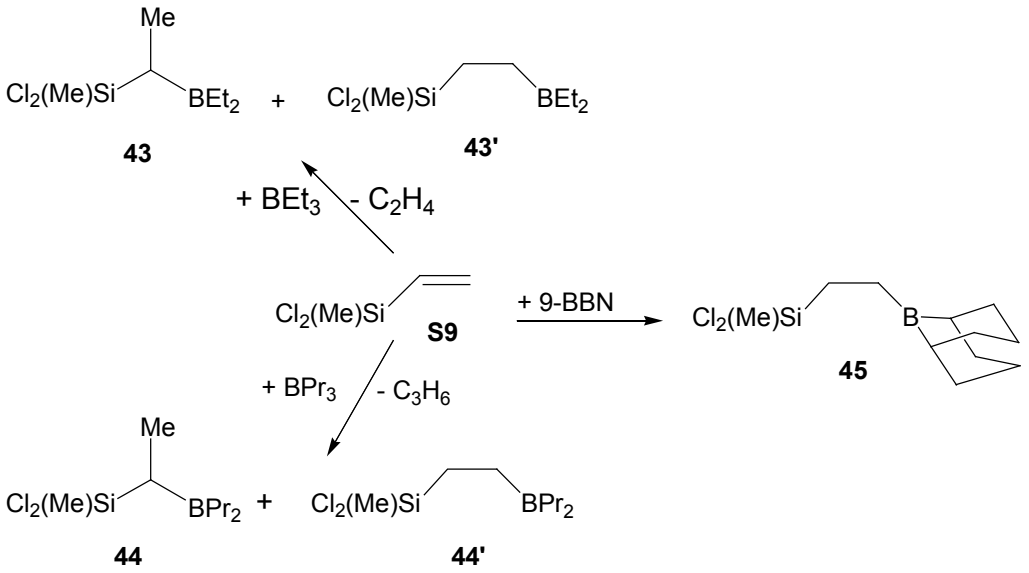
NMR spectroscopy

In Table 3.8 a conclusive set of NMR data belonging to silanes **40** and **41** is represented. The consistent data clearly indicate that all the three compounds **41a**, **c** and **42c** are similar to each other in structural aspects. The connectivity of various substituents is in a proper sequence. Such as the silyl and boryl groups are linked to the same carbon atom. This is evident from the broad ^{13}C NMR signal for olefinic carbon (B-C=)[97,98] and the sharp signal without ^{29}Si satellites for =CH carbon nuclei. For the ^{13}C(B-C=) NMR signal, $^{1}J(^{13}C,^{29}Si)$ can not be easily measured from ^{13}C NMR spectra. The ^{29}Si NMR spectra is a convenient mean to extract such information, provided that the spectra is run for sufficiently long time to get appropriate signal-to-noise ratio as in the case of **41c**. The $\delta\,^{29}Si$ is close to that of analogous silanes **41a** and **41c** which supports the suggested structure.

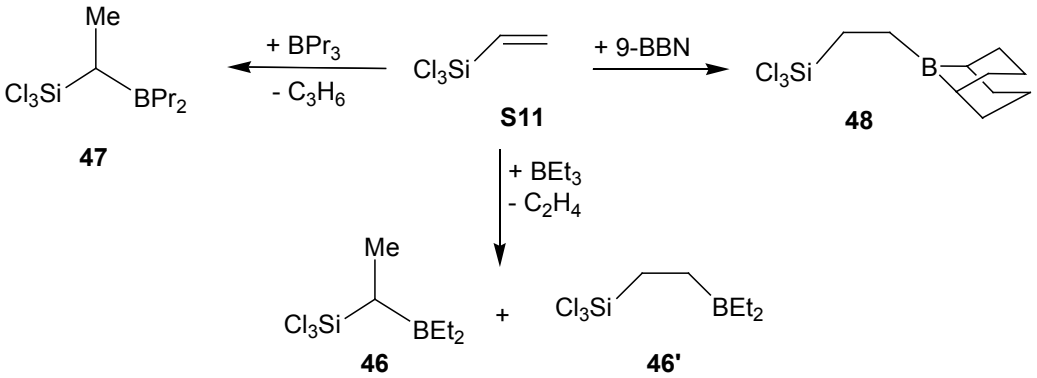
3.3. 1,2-Hydroboration reactions of vinylsilanes using BEt_3, BPr_3 and 9-BBN

Finally, the hydroborating potential of triethylborane was studied in reactions with the dichloro(methyl)(vinyl)silanes and trichloro(vinyl)silane (Scheme 3.9 and Scheme 3.10). Here it proved necessary to use heating up to 120 - 130 °C under pressure to induce the reaction with BEt_3. Mixtures of the hydroboration products **43**, **43´** and **46**, **46´** were obtained and could not be separated by distillation. The structural assignment follows unambiguously from the ^{1}H and ^{13}C NMR spectra (Table 3.9). The analogous result was found for BPr_3 to give **44**, **44´** and **47** under less harsh reaction conditions. Whereas **46** is the preferred product of the reaction of trichloro(vinyl)silane with BPr_3, BEt_3 affords slightly more of the isomer **46´** than the **46**. However, the results for BEt_3 and BPr_3 are not strictly comparable, since the reaction of BEt_3 with dichloro(methyl)(vinyl)silane, **S9** or trichloro(vinyl)silane, **S11** is accompanied by decomposition either of respective starting silanes or of the products. Using 9-BBN, one observes the hydroboration products **45** and **48** almost selectively (> 96 % according to NMR data), in agreement with the literature report for **48**.[114] Prolonged heating of **48** at 120 °C does not induce significant isomerization. Previous attempts at the hydroboration of trichloro(vinyl)silane[115,116]

using other hydroborating reagents gave mainly products analogous to **46** and **47**, similar to our results in particular to those for BPr_3.



Scheme 3.9. 1,2-haydroboration of dichloro(methyl)vinylsilane using BEt_3, BPr_3 and 9-BBN as hydroborating reagents.



Scheme 3.10. 1,2-Hydroboration of trichloro(vinyl)silane using BEt_3, BPr_3 and 9-BBN.

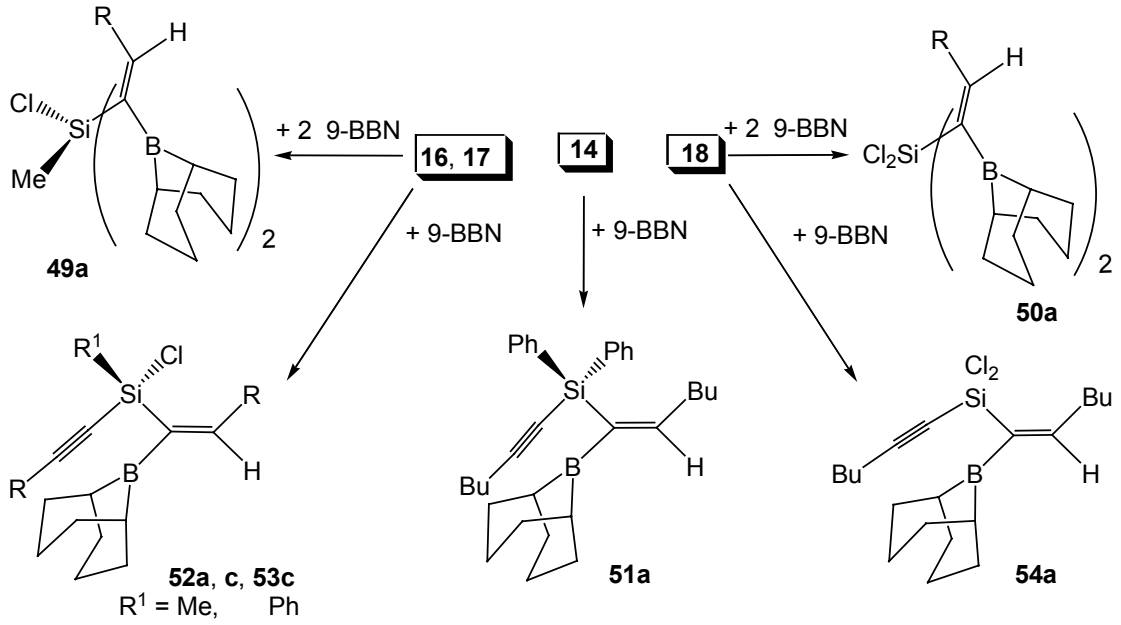
3.4. 1,2-Hydroboration of dialkyn-1-ylsilanes

Dialkyn-1-ylsilanes (**14** and **16 - 18**) were formed as side products of monoalkyn-1-ylsilanes (**3** and **5 - 7**). The purpose in studying their hydroboration reactions was to make use of these side products and to carry out some interesting reactions similar to the aforementioned chemistry. The products were expectedly boryl-substituted alkenylalkyn-1-yl silanes **51 - 54**. The silanes were prepared in two different ways (Scheme 3.11 and Scheme 3.12). Each method led to the expected

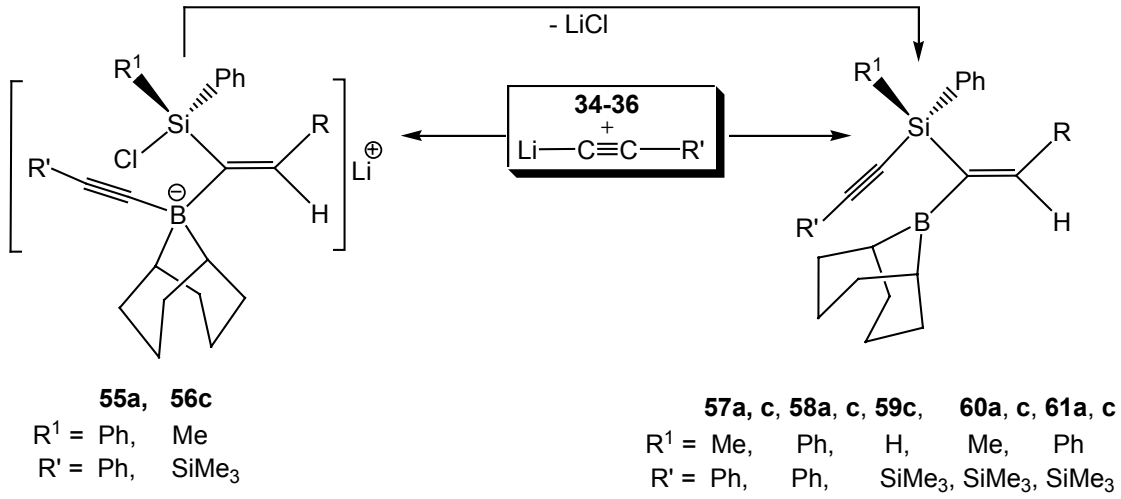
silanes and the desired compounds were obtained in good quantity (ca. 80 - 85 %, from NMR spectroscopy).

Procedure 1. The silanes **12 - 18** were treated with 9-BBN in 1:1 ratio at high temperature (80 - 100 °C). The reactions proceeded in a very controlled fashion leading to the desired products. The reactivities of some silanes were higher than the other and hydroboration of both alkyn-1-yl groups (Si-C≡C-) took place. Only two intermediates **49a** and **50a** were detected and fully characterized by NMR spectroscopy in solution. These compounds, di(alkenyl)silanes (**49a** and **50a**) are the ultimate products and do not undergo further transformations. The desired product obtained by the reaction of silane **14a** and 9-BBN (alkenyl(alkyn-1-yl)silane **51a**) is stable at room temperature and NMR spectroscopic data (^{1}H, ^{11}B, ^{13}C and ^{29}Si) could be collected. It was used in further reaction, *e.g.* for the formation of 1-silacyclobutene (*vide infra*). The experimental procedure for the syntheses of 1,1,1-(alkenyl)(alkyn-1-yl)(chloro)silanes (**52 - 54**) was almost the same. The only difference is the Si-Cl fuction which is not present in compound **51a**. Although this group (Si-Cl) is responsible for the decrease in reactivity of the Si-C≡C- bond, but does not affect the selecivity.

Procedure 2. The alkenylsilanes formed in previous reactions **34 - 36**, Scheme 3.6 are useful synthons for the alkenyl(alkyn-1-yl)silanes which turn into 1-silacyclobutenes afterwards. The reactivity is based on the replaceable Si-Cl function. Some reactions have been already addressed in several research articles[49,50,70,111] (Scheme 1.5). In the present work, the Si-Cl function was substituted by alkyn-1-yl group, to get the alkenyl(alkyn-1-yl)silanes similar to silanes **51 - 54** in structural and reactivity aspects. This method worked well and is more interesting as compared to **procedure 1**. Because there are many choices to include various organyl groups not only on silicon atom but also on -C=C- and Si-C≡C- groups. A solution of the respective alkenyl(chloro)silanes in hexane was added to freshly prepared alkynyl lithium in the same solvent at -78 °C. The reaction mixture was allowed to warm up to room temperature. After removal of solid and volatile materials the oily products left behind were identified as the desired silanes **57 - 61** (Scheme 3.12).



Scheme 3.11. 1,2-Hydroboration of dialkyn-1-ylsilanes.



Scheme 3.12. Substitution of the Si-Cl by an alkyn-1-yl group to afford either alkenyl(alkyn-1-yl)silanes or mixture containing borate-like intermediates.

There are two electrophilic centres present in alkenylsilanes **27 - 29**, one at the silicon and the other at the boron atom. Hence, the reaction of these silanes with Li-C≡C-Ph and Li-C≡-$SiMe_3$ could lead either to alkyn-1-ylborates **55a**, **56c** or directly to alkyn-1-ylsilanes **57 - 61** by elimination of LiCl. As shown in Scheme 3.12, borate intermediates **55a** and **56c** were detected in solution prior to elimination of LiCl. They eliminate LiCl at room temperature very slowly, accompanied by migration of the alkynyl group from boron to silicon atom to afford the desired alkenyl(alkyn-1-

yl)silanes **57 - 61**. Borate intermediates were not detected in all the cases although the same experimental procedure was experienced.

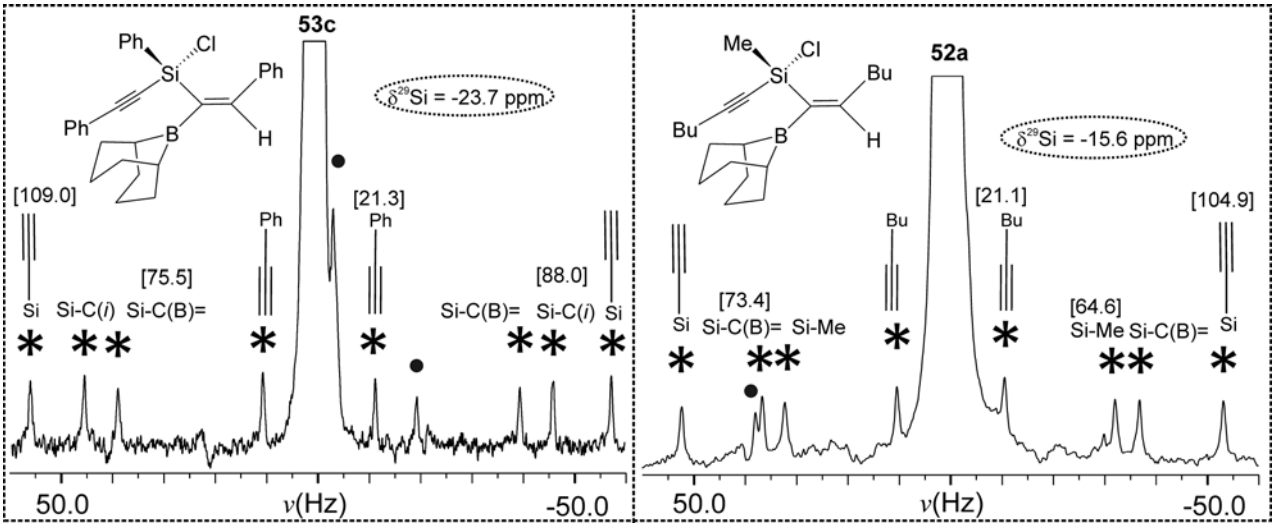


Figure 3.7. 59.6 MHz $^{29}Si\{^{1}H\}$ NMR spectra of alkenyl(alkyn-1-yl)silanes **52a** (right) and **53c** (left), expansions are given, showing ^{13}C satellites correspond to $^{1}J(^{13}C,^{29}Si)$ and $^{2}J(^{13}C,^{29}Si)$ coupling constants. Impurities are marked by filled circles.

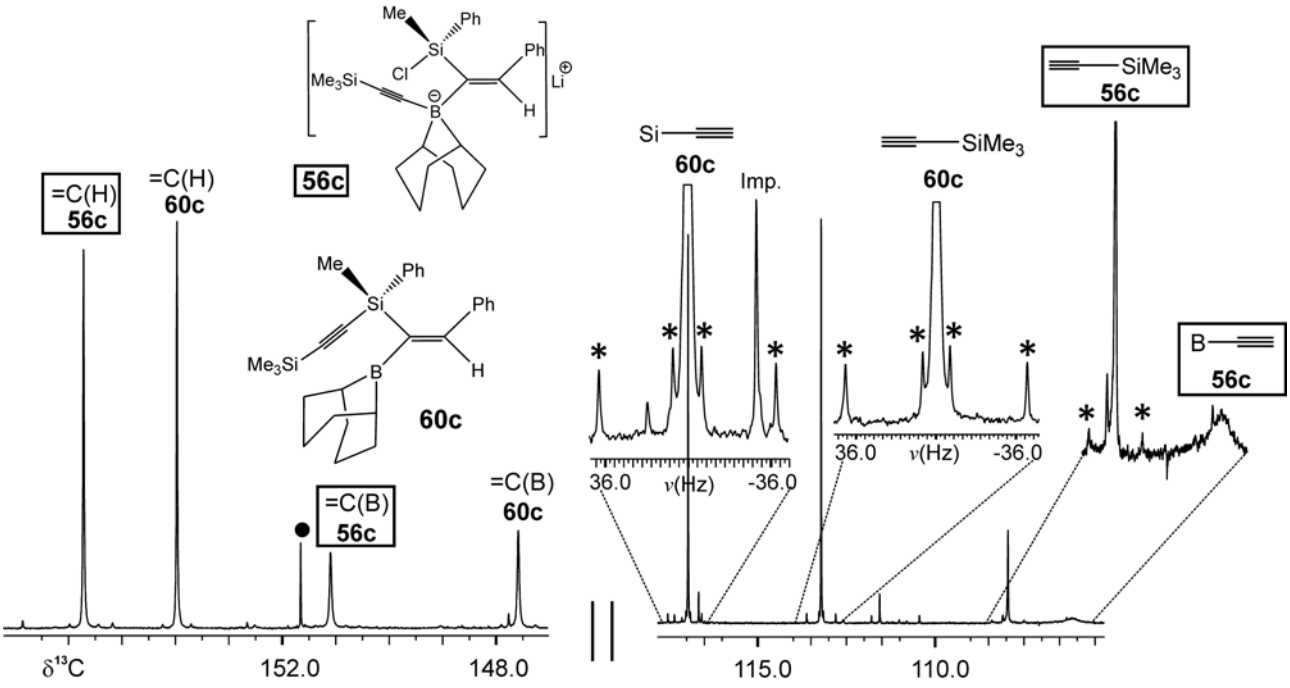


Figure 3.8. Part of $^{13}C\{^{1}H\}$ 100.4 MHz of mixture containing (alyn-1-yl)borate **56c** and alkyn-1-ylsilane **60c**. Expansions are given for carbon atoms showing ^{29}Si satellites marked by asterisks, correspond to $J(^{13}C,^{29}Si)$ spin-spin coupling constants. Signal marked by filled circle belong to 1-silacyclobutene

NMR spectroscopy

The NMR data (^{11}B, ^{13}C and ^{29}Si) belonging to side products, di(alkenyl)silanes **49a**, **50a** and alkyn-1-ylborate intermediates **55a**, **56c** are summarized in Table 3.10. All these silanes possess characteristic NMR data and could easily be distinguished from other products or intermediates in the reaction mixtures. In ^{13}C spectra of di(alkenyl)silanes, the vinyl group carbons (BC=CH) give a broad signal[97,98] for the carbon linked to boron atom and a sharp signal corresponding to (=CH) in the olefinic region. This region could be used as finger print region for such compounds.

In ^{1}H NMR spectra, the triplets in the olefinic region correspond to the =CH-Bu group and the additional signal in ^{29}Si NMR spectra at lower frequency than the respective alkyn-1-ylsilanes **52a** and **54a** leaves no doubt about the proposed structures. In contrast, the ^{11}B NMR spectra are less informative, as the resonance signal $\delta \approx$ 80 ppm could be observed for the desired products (**52a** and **54a**) as well as di(alkenyl)silanes **49a** and **50a** regarded as side products.

The alkyn-1-ylborate (**55a**, **56c**) detected in only two cases, serve as intermediates leading to alkenyl(alkyn-1-yl)silanes, **58a** and **60c**, respectively by elimination of LiCl. The NMR data regarding alkyn-1-ylborate intermediates are listed in Table 3.10. In these cases, the ^{11}B NMR data are very helpful as the resonance signals appear at δ = -16.5 and -16.8 ppm, respectively, typical of four-coordinated boron. In ^{13}C NMR spectra the alkyn-1-yl carbons are also indicative as ≡C-B is broadened owing to the partially relaxed ^{11}B-^{13}C spin-spin coupling. This signal has rather low intensity and could not be observed for **55a**. The Si-^{13}C≡ nuclei give rise to sharp signals with satellites for $^{1}J(^{13}C,^{29}Si)$ ca. 91.0 Hz. The other ^{13}C NMR signals were also observed within the expected range.

In the ^{29}Si NMR spectra, the signals are not too much shifted when compared with the starting silanes, since the ^{29}Si nuclei possess almost identical environments. On the other hand the alkyn-1-ylborate intermediates (**55a**, **56c**) and alkenyl(alkyn-1-yl)silanes (**58a**, **60c**) have distinct ^{29}Si chemical shifts on the basis of which alkyn-1-ylborates were proposed as reaction intermediates. With the passage of time the signals corresponding to alkyn-1-ylborate intermediates loose intensity, giving rise to the signals at lower frequency δ = –35.7 ppm (**58a**) and –33.1 ppm (**60c**) in the typical range for alkeny(alkyn-1-yl)silanes (Table 3.12). Physically the reaction could be monitored by the precipitation of LiCl in the NMR tube. At the same time, the ^{11}B

NMR signal at ca. δ –16 ppm looses intensity and the one at ca. δ 82 ppm gains intensity.

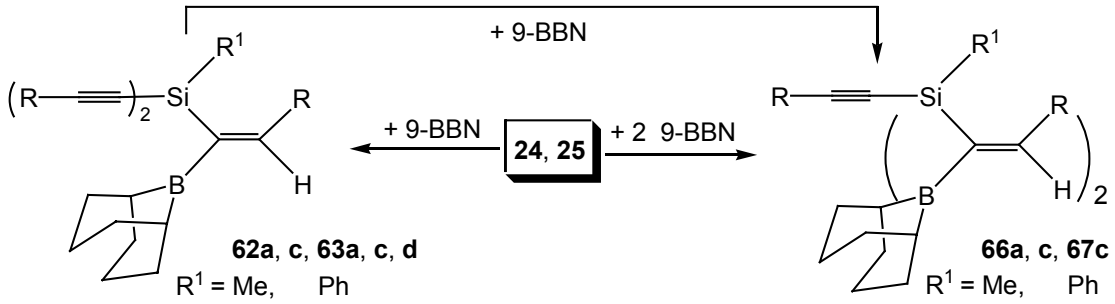
The NMR data (^{11}B, ^{13}C and ^{29}Si) pertinent to the alkeny(alkyn-1-yl)silanes **51-54** and **57 - 61** are given in Table 3.11 and Table 3.12, respectively. The silanes serving as intermediates for further transformations, **51 - 54** and **57 - 61** can readily be identified by their typical NMR data (Figure 3.8 for ^{13}C NMR of the mixture of three silanes **56c**, **60c** and silacyclobutene (*vide infra*). There are four fundamental ^{13}C NMR signals (Si-C≡C and B-C=CH) for proposing the given structures (Scheme 3.11 and Scheme 3.12). The former can be identified from typical ^{29}Si satellites in ^{13}C spectra, while the latter group gives a sharp (=CH) and a broad (B-C=) signal. In case of B-C=, the coupling constant $^{1}J(^{13}C,^{29}Si)$ can not be measured from the respective ^{13}C spectra. The ^{29}Si NMR spectra (Figure 3.6) of some compounds were measured for sufficiently long time to reach the appropriate signal-to-noise ratio for measuring the $^{1}J(^{13}C,^{29}Si)$ values. Also ^{29}Si NMR is here again of great importance for the confirmation of coupling constants obtained from ^{13}C spectra.

The alkenyl(alkyn-1-yl)silanes (**51 - 54** and **57 - 61**) were prepared by two different methods. The treatment of dialkyn-1-ylsilanes with 9-BBN (1:1 ratio) affords the alkenyl(alkyn-1-yl)silanes **51 - 54**. The ^{29}Si NMR signals were shifted by 15 - 20 ppm to lowfield (high frequency). In the case of alkenyl(alkyn-1-yl)silanes **57 - 61**, the shift was in opposite direction and the same signal was shifted by 15 - 20 ppm to upfield (lower frequency) with respect to starting alkenyl(chloro)silanes (for comparison see Table 2.1and Table 3.11).

3.5. 1,2-Hydroboration of trialkyn-1-ylsilanes

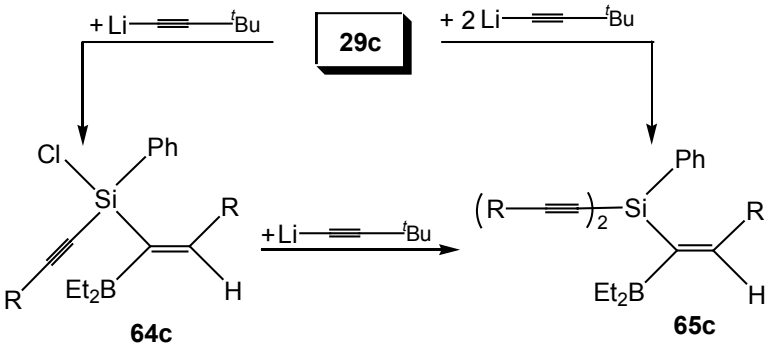
Trialkyn-1-ylsilanes are useful synthons for further transformations, *e.g.* 1-alkyn-1-yl-1-silacyclobutenes and 1-(alkenyl)-1-silacyclobutenes. The trialkyn-1-ylsilanes **24a**, **c** were treated with 9-BBN in 1:1 ratio. The reactions proceed selectively and afford a mixture of products **62**, **66** (Scheme 3.13). These silanes were accompanied by some rearranged products (1-silacyclobutene derivatives). Owing to more than two components of the mixture it was not easy to assign correctly all signals in the NMR spectra (^{13}C and ^{1}H). ^{29}Si NMR spectroscopy proved to be a powerful technique, for proposing intermediates (Figure 1.2). All the compounds *e.g.* **62**, **66** and silacyclobutenes derivatives possess characteristic ^{29}Si chemical shifts and they could readily be identified in the mixtures. The same reaction was carried out for one equivalent of silane **25** with one equivalent of 9-BBN.

It was observed that the 1,2-hydroboration is not an easy process as in case of **24** and compound **63** was formed in almost quantitative yield along with a very small amount of **67**. It was concluded that the Si-Ph group reduces the reactivity, hence, allowing for quantitative hydroboration of only one Si-C≡C- group on treatment with 9-BBN.



Scheme 3.13. Reaction of trialkyn-1-ylsilanes with 9-BBN as hydroborating reagent.

An alternative method proved to be fruitful for the synthesis of the desired akenyl(alkyn-1-yl)silanes. The hydroboration product (obtained by treatment of **6c** with BEt_3 at high temperature for several days), **29c** and other analogus alkenes are useful starting materials for several heterocyclic systems *e.g.,* 1-silacyclobutenes and borolenes (*vide infra*). The same experimental work up was adopted, as for the formation of alkenylsilanes **57 - 61**, to get 1,1,1-alkenyl(alkyn-1-yl)(chloro)silane **64** and alkenyl(dialkyn-1-yl)silane **65**. The silane **29c** was treated with freshly prepared 3,3-dimethyl-1-butynyl lithium in 1:2 ratio at –78 °C. After removal of soild and volatile materials the oily compound left, exhibited a mixture of compounds (Figure 3.8) presented in Scheme 3.14 and final products (1-silacyclobutene, *vide infra*) as a result of intramolecular rearrangement, 1,1-vinylboration.



Scheme 3.14. Conversion of alkenylsilane into alkenyl(dialkyn-1-yl)silane as a result of Si-Cl function replacement.

NMR spectroscopy

The NMR spectroscopic data (^{11}B, ^{13}C and ^{29}Si) for silanes **62 - 67** are listed in Table 3.13 and ^{1}H NMR data in Experimental section. The NMR data set is consistent with the proposed structures. Structural assignments were readily based on coupling constants $J(^{13}C,^{29}Si)$ especially for the Si-C≡C- unit and the broad ^{13}C (BC=) NMR signal.[97,120] The coupling constants $J(^{13}C,^{29}Si)$ in ^{13}C NMR spectra could be confirmed by observing ^{13}C satelite signals in the ^{29}Si NMR spectra of the respective compound (Figure 3.9). From the same figure it can be deduced that all compounds of the mixture possess distinct ^{29}Si chemical shifts and the reaction mechanism and various intermediates could be proposed. These facts make the mechanism of the reaction straightforward, the data listed in Table 3.13 are quite sufficient for structural elucidation of the title compounds in solution state.

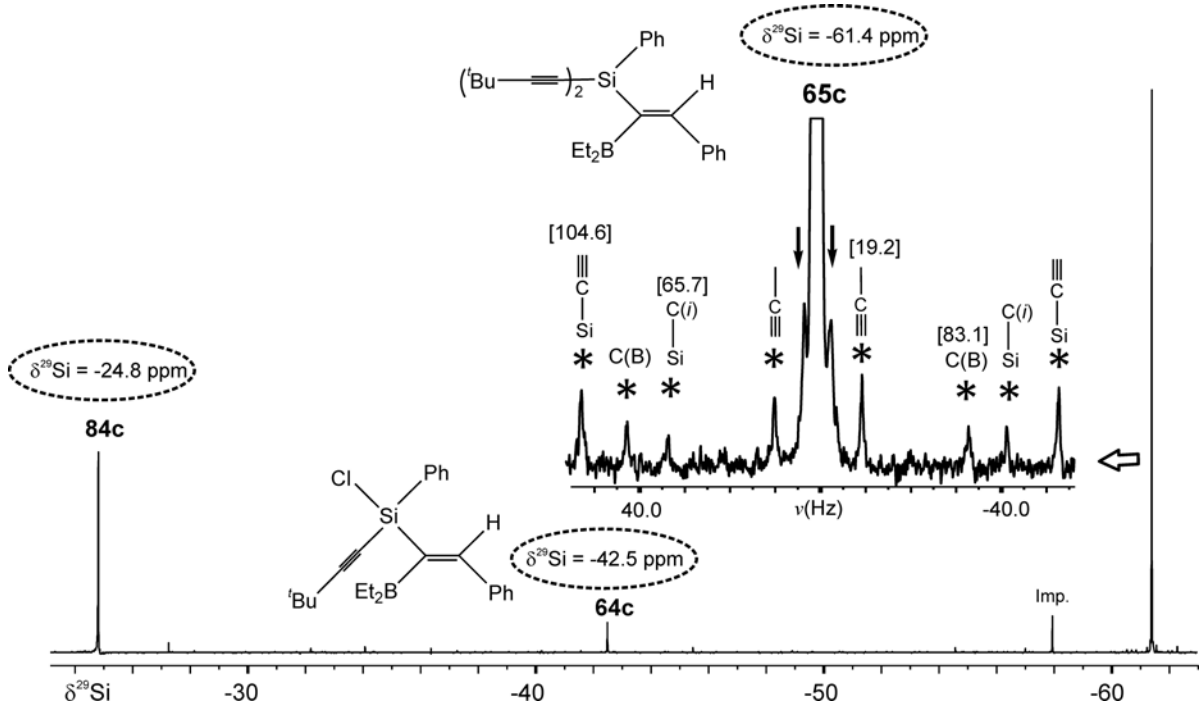
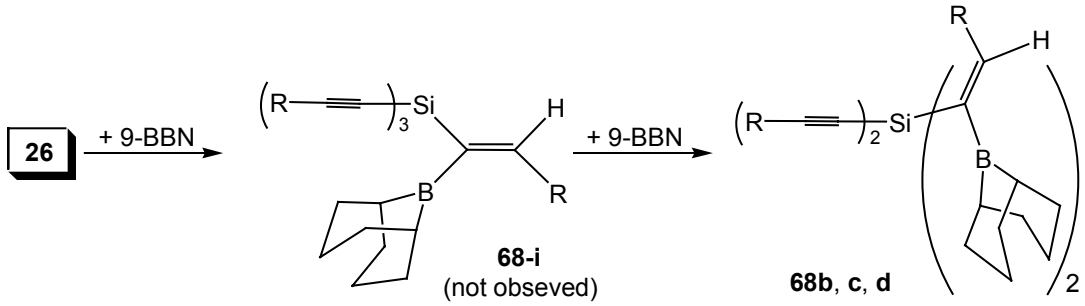


Figure 3.9. 59.6 MHz ^{29}Si{^{1}H} NMR spectra mainly contain the alkenyl(dialkyn-1-yl)silane **65c**, together with alkenyl(alkyn-1-yl)chlorosilane **64c** and 1-silacyclobutene derivative **84c**. Expansion is given for the main signal, showing ^{13}C satellites, marked by asterisks, further satellites are visible with a value of 5.9 Hz, are due to $^{n}J(^{13}C,^{29}Si)$ n ≥ 2.

3.6. 1,2-Hydroboration of tetraalkyn-1-ylsilanes using 9-BBN

All four Si-C≡C- bonds can equally participate in the reaction with 9-BBN, provided that sufficient amount of 9-BBN is present, *e.g.* in 1:4 ratio. However, this was not the destination during the course of this work. Our interest was focused to get the 1,1-(dialkenyl)-1,1-(dialkyn-1-yl)silanes **68b - d** (Scheme 3.15). In this context, one equivalent of the silane **26** was treated with two equivalents of 9-BBN. The reactions proceed in two steps, in the first step, silanes **68-i** (not detected), precursors of **68** are formed, on further reaction with one equivalent of 9-BBN intermediates **68-i** afford selectively the alkene derivatives **68b**-**d**. The compounds **68b** - **d** are not final products and serve as intermediates for further reactions (spiro-silanes, *vide infra*). All the compounds **68b** – **d** were fully characterized by multinuclear NMR spectroscopy (Table 3.14 and Experimental section).



Scheme 3.15. Twofold 1,2-hydroboration of tetraalkyn-1-ylsilanes in two steps.

NMR spectroscopic results

The ^{11}B, ^{13}C and ^{29}Si NMR data of compounds **68** are listed in Table 3.14 and ^{1}H NMR data are given in the Experimental part. The data set is fully consistent with the proposed structures. The ^{11}B chemical shifts are found within a range, typical of three-coordinated boron atoms in triorganoboranes. ^{29}Si NMR spectra[109,117] measured by using $^{1}H \rightarrow ^{29}Si$ polarization transfer from the olefinic protons, *e.g. via* INEPT pulse sequences,[118] serve for assigning intermediates and products. This assignment is supported by observing the respective ^{13}C satellite signals (Figure 3.10). The ^{13}C NMR spectra provide a wealth of information regarding the structures by characteristic chemical shifts, coupling constants $J(^{13}C,^{29}Si)$ and the broadened ^{13}C NMR signals for carbon atoms linked directly to ^{11}B nuclei (as a result of partially relaxed scalar ^{11}B-^{13}C spin-spin coupling[97,98]). In ^{1}H NMR data =CH signal obtained

as singlet with ^{29}Si satellites in olefinic region strongly supporting the proposed structures.

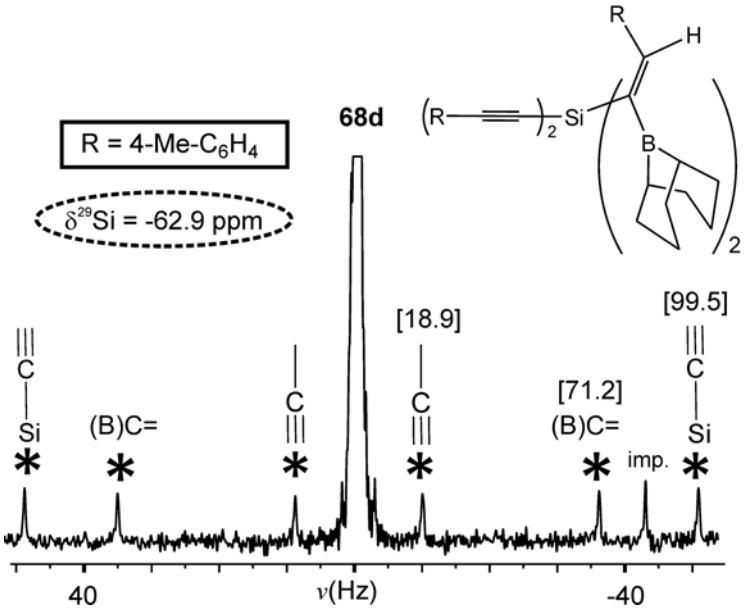


Figure 3.10. 59.6 MHz ^{29}Si{^{1}H} NMR spectra (refocused INEPT) of the intermediate **68d**, expansion for the signal shows ^{13}C satellites, marked by asterisks, corresponding to $^{1}J(^{13}C,^{29}Si)$ and $^{2}J(^{13}C,^{29}Si)$, further ^{13}C satellites are visible, close to the parent peak, which arise from $^{n}J(^{29}Si,^{13}C)$ ($n \geq 2$), with a coupling of 4.9 and 2.1 Hz.

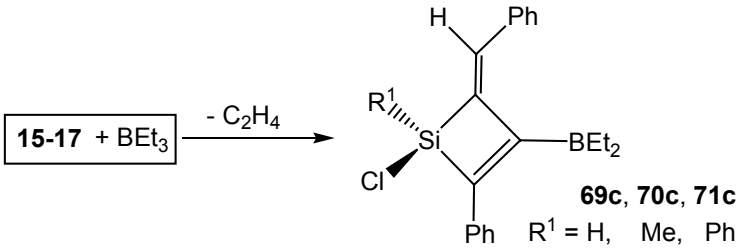
4. 1-SILACYCLOBUTENES

4.1. Reaction of dialkyn-1-yl(chloro)silanes with BEt_3 and BPr_3

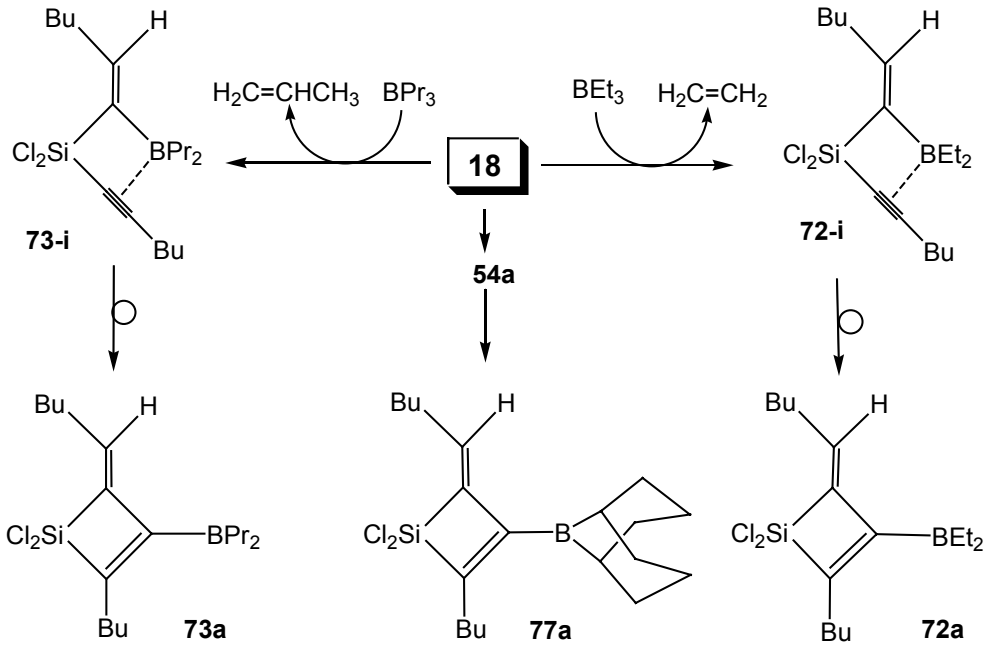
The comparison of the results in Scheme 3.1, Scheme 3.3 and Scheme 3.6 shows the influence of substituents upon Si-C≡ bond cleavage. It is known for the Si-Cl function that it stabilizes the Si-C≡ bond, in contrast to the Si-H function, and the 1,2-hydroboration pathway becomes an alternative to 1,1-ethylboration. Therefore, it was of interest to study the influence of a second Si-C≡C-Bu function. In this context dialkyn-1-yl(chloro)silanes (**15 - 17**) and dialkyn-1-yl(dichloro)silanes (**18a**) were treated (Scheme 4.1 and Scheme 4.2) with BEt_3 and BPr_3 at elevated temperature (100 - 120 °C) in a similar way as discussed for alkenylsilanes **27 - 33**. In these reactions a new route was followed, clean formation of 1-silacyclobutenes (**69 - 73**) *via* 1,2-hydroboration was observed. If hydroboration does not take place, then one expects clean formation of siloles as a result of 1,1-ethylboration. As has been observed in the case of dialkyn-1-ylsilanes with organic substituents on silicon atom (*e.g.* $Me_2Si(C{\equiv}C\text{-}R)_2$).[59,119] The reactions are straightforward if we consider 1,2-hydroboration as the first step. The reactions proceed in two steps, first an intermediate where 1,2-hydroboration of one Si-C≡C- bond takes place, followed by a fast step involving intramolecular 1,1-vinylboration. Owing to high temperature, the short-lived intermediates like **72-i** and **73-i**, were not detected in the reaction solutions. The reactions are regarded to proceed in the similar way as in the case of conventional 1,2-hydroborating reagent, 9-BBN. In the latter case the important intermediate **54a** was detected and studied in solution state by NMR spectroscopy.[102] The compounds represented in Scheme 4.1 and Scheme 4.2 are oily liquids and were characterized by NMR spectroscopy without further purification.

Here it is noteworthy that the reactivity of silanes bearing one Si-Cl function with BEt_3 (Scheme 4.2) depends upon the organyl group –C≡C-R. For such reactions there are two routes to be followed, 1,1-ethylboration as the usual route (reported so far) or 1,2-hydroboration (new finding in this work). Both 1,1-ethylboration and 1,2-hydroboration are followed by 1,1-vinylboration to afford either siloles or 1-silacyclobutenes, respectively. These silanes were proved to be border-line compounds, as they favoured both the products, i. e. siloles as well as 1-silacyclobutenes depending on -C≡C-R group. Here the influence of R = Ph group was the key factor which diverted the reactions in alternate direction (1-

silacyclobutenes). The results represented in Table 4.1 proved that, the formation of diethylboryl-substituted 1-silacyclobutenes are rare examples of combination of 1,2-hydroboration and 1,1-organoboration, without using a boron hydride reagent.[70] The straightforward access to 1-silacyclobutenes opens the way to novel heterocycles taking advantage of the reactivity of the Si-Cl and in some cases Si-C≡C-Ph functions.



Scheme 4.1. 1,2-Hydroboration a favoured route adopted by dialkyn-1-yl(chloro)-silanes with BEt_2



Scheme 4.2. Formation of 1-silacyclobutenes, first examples of 1,2-hydroboration using BEt_3 and BPr_3 as hydroborating reagents.

NMR spectroscopic studies

The NMR data correspond to 1-silacyclobutene **69 - 73** together with **77a** (for comparison) are listed in Table 4.1. The compound **77a** was synthesized by the reaction of dialkyn-1-ylsilane with a well known hydroborating reagent, 9-BBN. The

NMR data of all the compounds are not only closely related to each other but also well comparable with the data reported for 1-silacyclobutenes bearing two organic moieties on silicon, i.e. Me_2Si- and Ph_2Si-.[70,111] More information can be obtained from ^1H NMR spectroscopy where triplets for =CH(Bu) group (**69a, 73a, 77a**) and singlets for =CH(Ph) protons (not assigned in all cases, **70c - 72c**) were observed in olefinic region. In the aliphatic regions a triplet and a broad quartet can be seen only for -BEt_2 group and no signals were observed for another Et group.

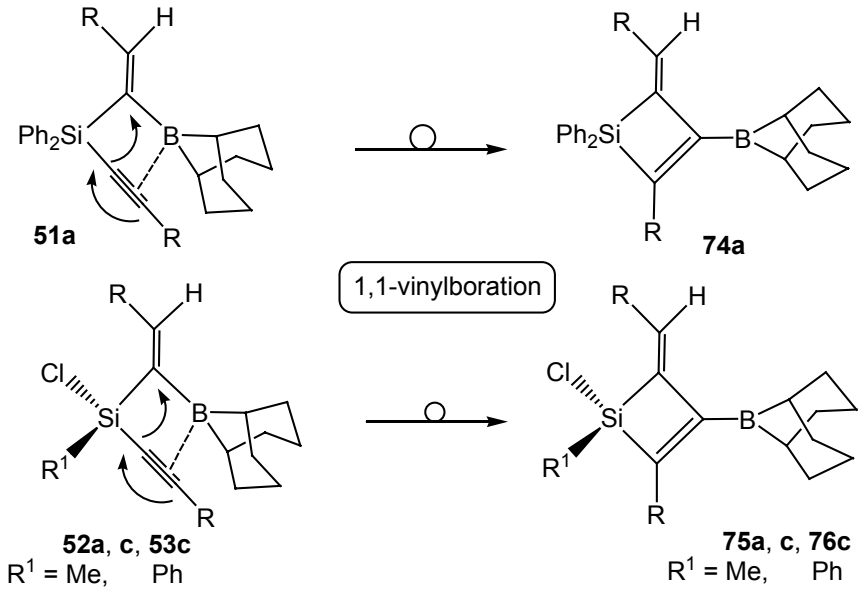
In the ^{13}C spectra all signals belonging to ring carbons can be assigned unambiguously based on the ^{29}Si satellites for coupling constants $^1J(^{13}C,^{29}Si)$ (C-2, C-4) and typically broad ^{13}C(B-C=) NMR signal (C-3).[97,98] All other ^{13}C NMR signals are within the expected range.[111] The spectra are more informative in aliphatic region. There are no ^{13}C resonance signals for ethyl groups except of BEt_2 which is only possible if 1,1-ethylboration *does not* take place. The absence of additional ethyl resonance signals leaves no doubt about 1,2-hydroboration using commercial BEt_3. The same was observed for BPr_3.

4.2. Conversion of BBN-substituted alkenyl(alkyn-1-yl)silanes into 1-silacyclobutenes

The boryl-substituted alkenyl(alkyn-1-yl)silanes undergo further rearrangement to afford 1-silacyclobutenes. The formation of 1-silacyclobutenes *via* 1,2-hydroboration followed by intramolecular 1,1-organoboration has been addressed in a single paper.[70] In the said report some information regarding intermediates (full NMR data set) and solid state structures are missing. Reactions of alkyn-1-ylsilanes were carried out with the hope, to get single crystals suitable for X-ray structure analysis in order to get structural information in solid state and to collect complete set of NMR data for intermediates (i.e. **55a, 56c** and **57 - 60**). The work was initiated with bulky group, such as phenyl (Ph) in order to get the required data. All missing information were achieved.[111] Moreover, two different methods were introduced to get the desired compounds.

Method 1: The silanes **51 - 53** discussed already, bears two reactive functional groups, diorganoboryl (9-BBN) and alkyn-1-yl group. Owing to the presence of these two groups the silanes **51 - 53** undergo further transformation, *e. g.* intramolecular 1,1-vinylboration. These intermediates were heated at 80 - 120 °C in benzene or toluene as solvents to afford the desired heterocycles, the 1-silacyclobutenes **75 - 77** (Scheme 4.3). The reactions proceed smoothly and clean products could be obtained

if 9-BBN is used in 1:1 ratio. Under controlled reaction conditions hydroboration of only one Si-C≡C- bond occurs. In contrast the presence of an excess of 9-BBN causes the hydroboration of the second alkyn-1-yl group and leads to side products, i. e. di(alkenyl)silanes **49a** and **50a**. This method is useful for the synthesis of 1-silacyclobutenes bearing Si-Cl or $SiCl_2$ functional groups.

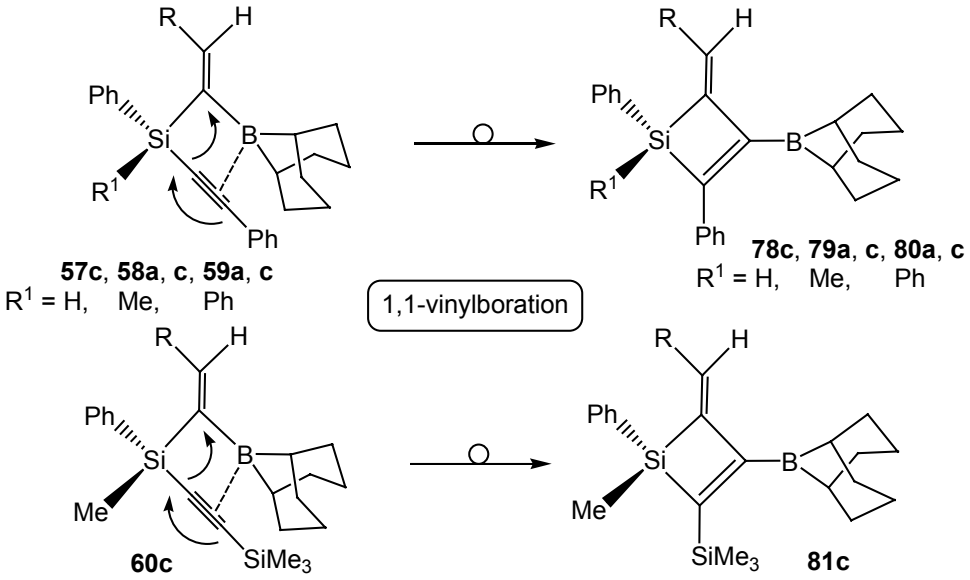


Scheme 4.3. Formation of 1-silacyclobutene derivatives from alkenyl(alkyn-1-yl)silanes

Method 2: This method is better than the previously discussed (**Method 1**) in the sense, different as well as identical substituents on ring carbons (C-2 and C-4) can be included. The starting silanes (**1 - 3**) bear only one Si-C≡C- function, and therefore, the purification of the starting materials is easy. It is easy to substitute the Si-Cl function in silanes (**35**, **36**) by alkynyl group. Once the alkenyl(alkyn-1-yl)silanes (**57** - **59)** are obtained, they undergo transformation as **75 - 77** under the given reaction conditions as discussed in **Method 1**. Following this method some borate-like intermediates were characterized, serving as precursors of **57 - 59** on elimination of LiCl, and at the same time -C≡C-Ph or -C≡C-$SiMe_3$ bond shifts from B to Si atom. Although the borate-like intermediates were not detected in all reactions, two of them (**55a**, **56c**) were characterized, these intermediates are helpful in exploring the complete reaction mechanism for he formation of 1-silacyclobutenes.

Both the methods (**1** and **2**) explained above afford 1-silacyclobutenes with a variety of organic groups. Each method has some limitations *e.g.,* in **Method 1**, the di(alkenyl)silanes were side products, they do not undergo dehydroboration to afford

1-silacyclobutenes and purification of starting silanes (R^1_2Si-$(C{\equiv}C$-$R)_2$) bearing larger substituents, *e. g.* $Ph_2Si(C{\equiv}C$-$Ph)_2$, are serious drawbacks of this method. On the other hand following **Method 2**, 1-silacyclobutenes bearing Si-Cl function(s), (using (chloro)silanes as starting materials) can not be obtained in pure state. As there are equal chances of replacement of more than one Si-Cl functions by alkynyl groups. The ring closure was not satisfactory in the case of -$SiMe_3$ group under the same reaction conditions.



Scheme 4.4. 1-Silacyclobutenes bearing different groups on C-2 and C-4.

The overall output was satisfactory and all the required information was extracted. All the compounds i.e., starting silanes, intermediates and 1-silacyclobutenes are stable and were studied by multinuclear NMR spectroscopy in solution state and X-ray structure of **80a**[111] was determined in solid state.

NMR spectroscopic studies

The ^{11}B, ^{13}C and ^{29}Si NMR data of 1-silacyclobutenes **74 - 76** and **78 - 81** are collected in Table 4.2 and ^{1}H NMR data are represented in Experimental section. These compounds were synthesized following two parallel routes. The data set is consistent with the proposed structures. The ^{11}B chemical shift in the range of δ = 82 - 89 ppm, is typical of three-coordinated boron atoms. The ^{29}Si NMR spectra were measured, using INEPT[118] pulse sequence with ^{1}H-decoupling, based on $^{3}J(^{1}H_{=CH}, ^{29}Si)$ = 20 - 35 Hz. It was particularly useful in monitoring the progress of the

reactions and detection of intermediates. In ^{13}C NMR spectra, the ^{13}C(C-2, C-4) NMR signals possess ^{29}Si satellites and ^{13}C(BC-3) is typically broad at highest frequency ($\delta \approx 180$ ppm). All ^{13}C NMR signals for R and R^1 were found within the expected range. In some compounds like **76c** and **77a** the rotation of CBC plane of 9-BBN is restricted which is evident from relevant ^{13}C NMR signals. The 1-silacyclobutene derivatives achieved were either oily liquids or waxy solids. One member (**80a**) of the series was crystalline and a suitable single crystal was studied by X-ray crystallography.

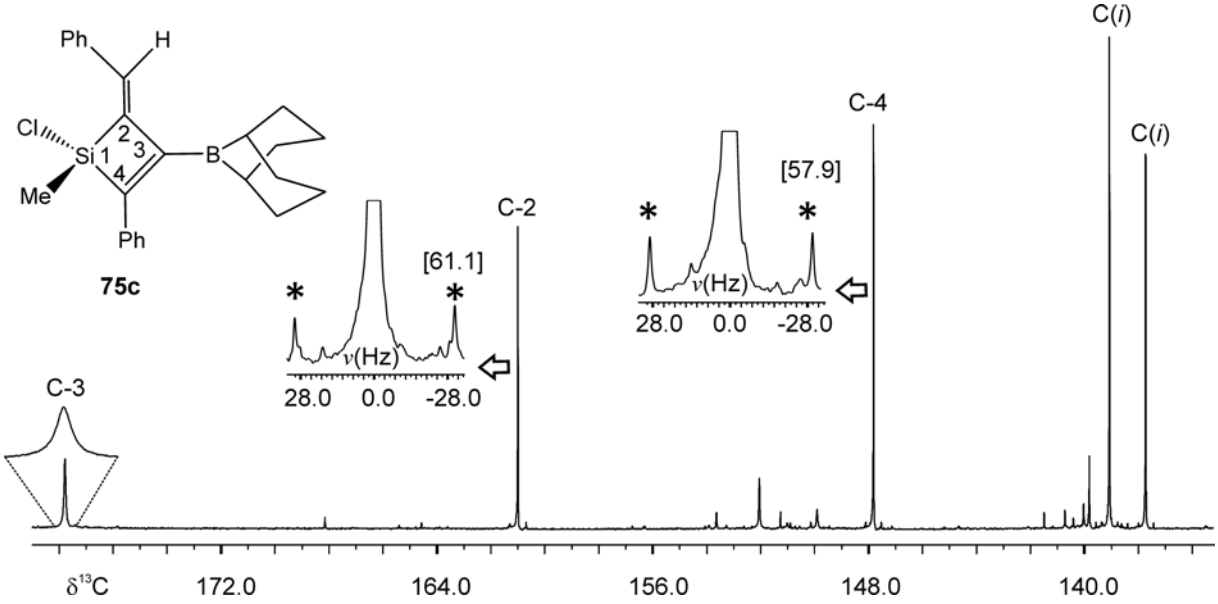


Figure 4.1. Part of 100.5 MHz $^{13}C\{^1H\}$ of reaction mixture mainly contains 1-silacyclobutene **75c**. Expansions are given for the C-2 and C-4 showing ^{29}Si satellites corresponding to $^1J(^{13}C,^{29}Si)$ coupling constants. The broad signal for C-3 bonded to ^{11}B, is due to ^{11}B-^{13}C partially relaxed scalar coupling.

*X-ray analysis of the 1-silacyclobutene **80a***

The molecular structure of 1-silacyclobutene **80a** along with selected structural parameters is given in Figure 4.2. The data relevant to crystal structure determination are listed in Table 4.3. Intermolecular as well as intramolecular contacts are negligible. There is an expectedly acute endocyclic bond angle C-Si-C = 74.76(7)°. The C=C bonds (endocyclic and exocyclic) are almost exactly in the same plane therefore, the four-membered ring is planar within the experimental error. The CBC-plane of 9-BBN group is oriented almost perpendicular (85.3°) to the 1-silacyclobutene plane. This is an ideal situation for hyperconjugation involving C-C σ

bonds and the empty p_z orbital of the boron atom.[120 - 123] Indeed, the elongated bond lengths of C15=C16 (137.4 (2) pm), when compared with the other double bond C12=C13 (132.6 (2) pm) may be interpreted in this way. The plane of the phenyl group bonded to C16 is only slightly twisted by 4.6° against the plane of the four-membered ring. All other bond lengths and angles appear to be in the expected ranges.

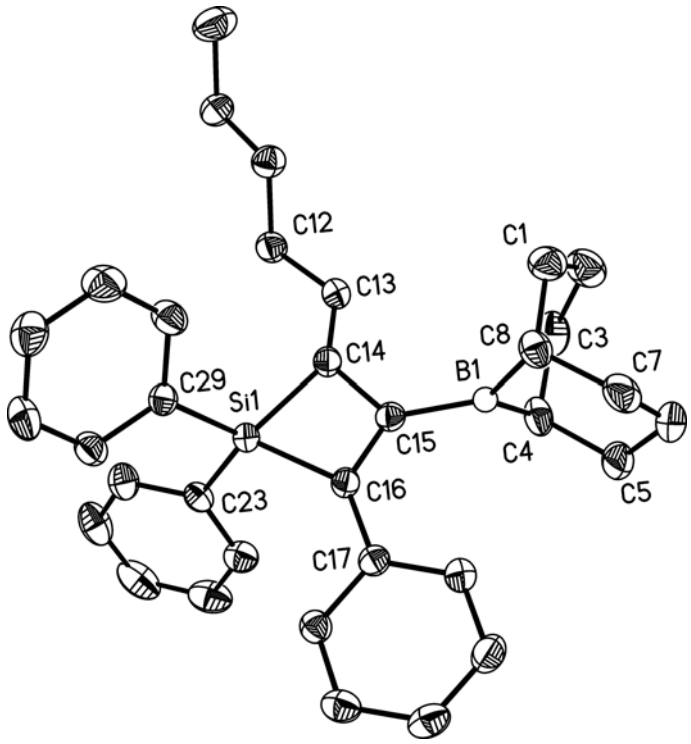
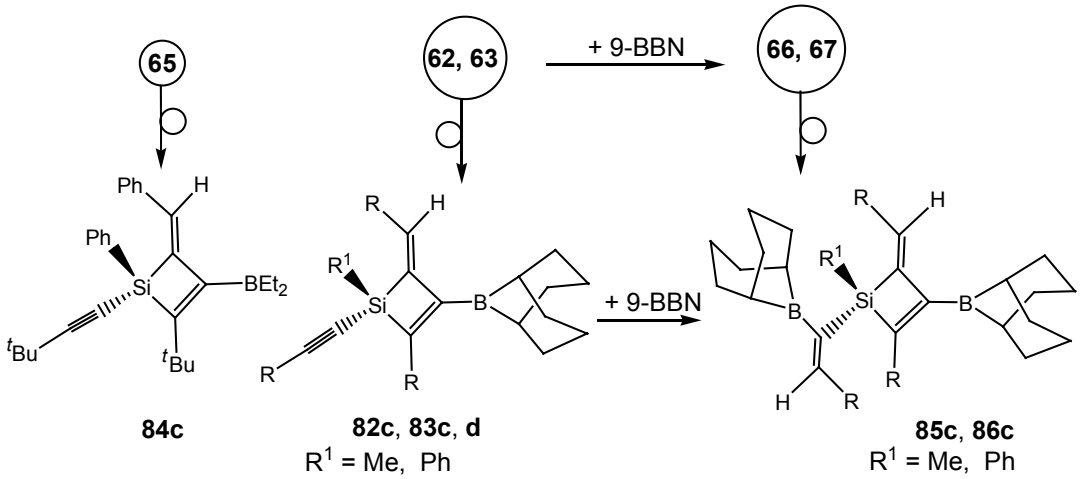


Figure 4.2. Molecular structure of 1-silacyclobutene **80a**, ORTEP plot (50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (pm) and bond angles (deg.): C13-C14 132.6 (2), C14-C15 149.6 (2), C14-Si1 187.4 (16), C15-C16 137.4 (2), C15-B1 156.1 (2), C16-C17 145.5 (2), C16-Si1 185.9 (15), C23-Si1 187.2 (16), C29-Si1 186.6 (16), C13-C14-C15 130.2 (15), C15-C14-Si1 88.3 (10), C16-C15-C14 104.2 (13), C15-C16-C17 129.8 (14), C15-C16-Si1 92.7 (10), C16-Si1-C29 119.5 (7), C16-Si1-C23 114.4 (7), C29-Si1-C23 109.8 (7), C16-Si1-C14 74.8 (7).

4.3. Alkyn-1-yl- and alkenyl-substituted 1-silacyclobutenes

The alkenyl(dialkyn-1-yl)silanes **62**, **63**, **65** and dialkenyl(alkyn-1-yl)silanes **66**, **67** lead to 1-(alkyn-1-yl)-1-silacyclobutenes **82 - 84** or 1-(alkenyl)-1-silacyclobutenes **85** and **86**. The product distribution in the mixture depends upon various factors, *e. g.* reaction temperature and nature of R and R^1 groups. The 1,2-hydroboration of only one Si-C≡C- bond takes place almost quantitatively (90 %, from NMR spectroscopic data) in the case of tri(phenylethynyl)(phenyl)silane **25c** leading to dialkyn-1-ylsilane

63c and finally to alkyn-1-yl-substituted 1-silacyclobutene **83c**. The reaction of tri(phenylethynyl)(methyl)silane **24c** with 9-BBN affords a mixture, containing silane **62c**, where hydroboration of one Si-C≡C- group takes place and **66c**, where hydroboration of two Si-C≡C- functional groups occurred in almost 40 : 60 % (Figure 4.3). Finally the intramolecular 1,1-vinylboration lead to 1-silacyclobutenes **82c** and **85c**, respectively (Scheme 4.4). No reaction with threefold 1,2-hydroboration was observed. The heterocycles achieved in these reactions are oily liquids and could readily be identified from their characteristic NMR data (^{11}B, ^{13}C, ^{1}H and ^{29}Si).



Scheme 4.5. Formation of 1-silacyclobutes bearing Si-C≡C and Si-C=C functional groups.

The silane **29c** bears two Si-Cl functional groups which makes it more attractive for further studies. It was treated with two equivalents of 3,3-(dimethyl)butyn-1-yl lithium (Li-C≡C-^{t}Bu) to afford mainly the intermediate **65c** and afterwards 1-(3,3-dimethylbutyn-1-yl)-1-silacyclobutene **84c** *via* intramolecular 1,1-vinylboration. The final products were waxy solids and were characterized by multinuclear NMR spectroscopy in solution.

NMR spectroscopic studies

The NMR data (^{11}B, ^{13}C and ^{29}Si) of 1-silacyclobutene derivatives are listed in Table 4.4. The NMR data set is consistent with the proposed structures. ^{29}Si NMR spectroscopy is particularly important in assignments, as the compounds in the mixture (intermediates and final products) possess distinct ^{29}Si chemical shifts. The data obtained mainly for four-membered ring (1-silacyclobutene) are well comparable with that of 1-silycyclobutenes **75 - 81**. In ^{13}C NMR spectra, the substituents on the

silicon atom Si-(B)C=C and Si-C≡C- can be readily assigned, based on ^{29}Si satellites for the ^{13}C(Si-C≡C) signals, whereas a sharp ^{13}C(=CH) and a broad ^{13}C(B-C=) signal[97,98] at high frequency is characteristic of the exacyclic C=C(B) group. Other NMR data are within the expected range.

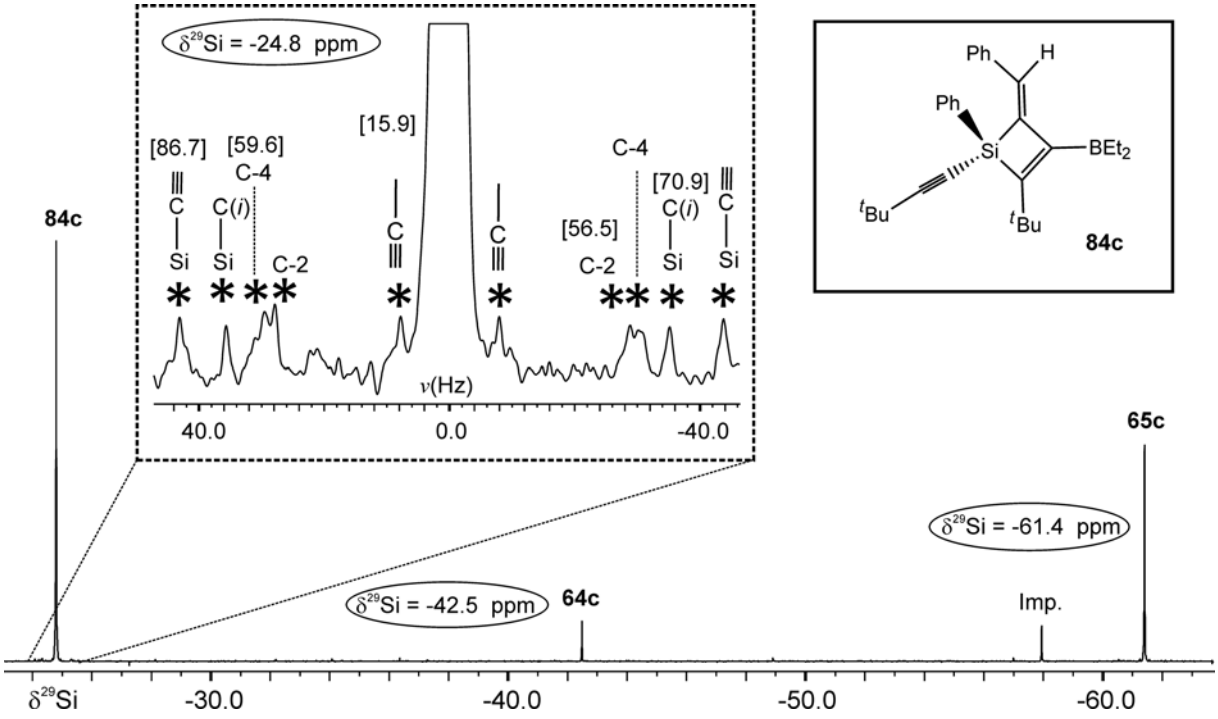
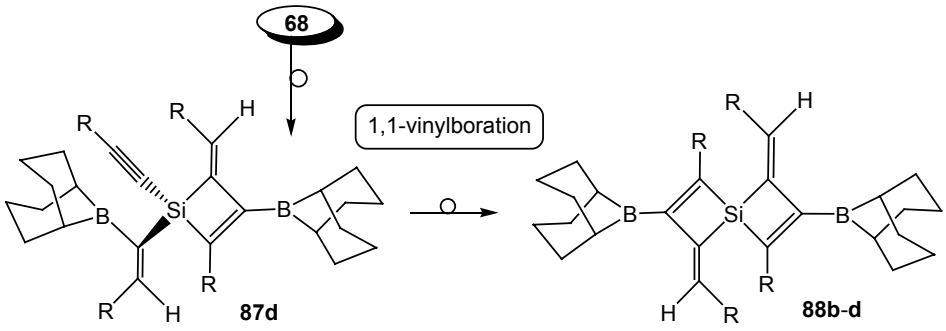


Figure 4.3. 59.6 MHz ^{29}Si{^{1}H} NMR spectra (refocused INEPT) showing the intermediate **64c**, **65c** (see also Figure 3.8 for expansion of **65c**) and final product **84c**. An expansion (inserted) is given for the main signal belong to **84c**, showing satellites marked by asterisks, representing ^{1}J(^{13}C,^{29}Si) and ^{2}J(^{13}C,^{29}Si).

4.4. 4-Silaspiro[3.3]hepta-1,5-diene derivatives

The formation of spirosilanes is the result of twofold 1,2-hydroboration followed by successive intramolecular twofold 1,1-vinylboration. It has been shown that 1,2-hydroboration and 1,1-organoboration are completely different type of reactions. Both of these reactions require totally different reaction conditions. 1,2-hydroboration is an easy process and takes place in short time at high temperature or even at room temperature in several cases.[45,70] Conversely the 1,1-organoboration is a slow reaction and requires harsh reaction conditions, *e. g.* heating at high temperature (80-120 °C) for several days.[29] Alternatively an easy and fast 1,1-organoboration occurs if a boryl group is introduced into a molecule bearing at least one Si-C≡C- functional group, by other way such as 1,2-hydroboration. The formation of the four-

membered ring is the result of the combination of 1,2-hydroboration and 1,1-organoboration. In the light of experience gained so far, silanes **26b** - **d** were treated with two equivalents of 9-BBN, affording intermediates **68b - d**. It was expected that these intermediates will undergo successively twofold 1,1-vinylboration and will afford spirosilanes. In this context, they were treated in the same way as silanes **82 - 86**. The samples were heated in benzene or toluene at 80 - 120 °C, the reactions lasted ranging from few hours (**88b**, **c**) to a couple of days (**88d**).



Scheme 4.6. Formation of spirosilanes, as a result of successive twofold 1,2-Hydroboration followed by 1,1-vinylboration.

The reactions could be conveniently monitored by ^{29}Si NMR spectroscopy since products and intermediates possess distinct chemical shifts $\delta\,^{29}$Si (Figure 3.9, Figure 4.4, Table 3.13 and Table 4.5). It was concluded that the rearrangement takes place in two steps. In the first step a four-membered ring is formed followed by the next step of ring closure (Figure 4.4). The spirosilanes **88b - d** are air-sensitive waxy (**88b**) or crystalline solids (**88c**, **88d**), of which **88d** could be crystallized to give single crystals suitable for X-ray structural analysis (Figure 4.6).

NMR spectroscopic results

The ^{11}B, ^{13}C and ^{29}Si NMR data of the compounds **88b - d** are listed in Table 4.5 and ^{1}H NMR data are given in Experimental section. The data set is fully consistent with the proposed structures. The chemical shifts $\delta\,^{11}$B are found within a small range, characteristics of three-coordinate boron atoms in triorganoboranes with little or negligible BC(pp)π interactions.[110] Therefore, it can be assumed that the orientation of the BC_2 plane of the 9-BBN unit is preferably perpendicular to the four-membered ring. ^{29}Si NMR spectra[109,117] measured by using ^{1}H$\rightarrow^{29}$Si polarization transfer from the olefinic protons, *e. g, via* INEPT pulse sequences,[118] serve for the

assigning intermediates and products. The ^{13}C NMR spectra provide a wealth of information about the proposed structures by characteristic chemical shifts, coupling constants $J(^{13}C,^{29}Si)$ and the broadened ^{13}C(B-C) NMR signals.[97,98] As can be deduced from the ^{11}B NMR spectra, the boryl group prefers an orientation perpendicular to the four-membered ring, evident by the ^{13}C(9-BBN) signals, typical of restricted rotation about the (C-2,6)B bond (Figure 4.5).

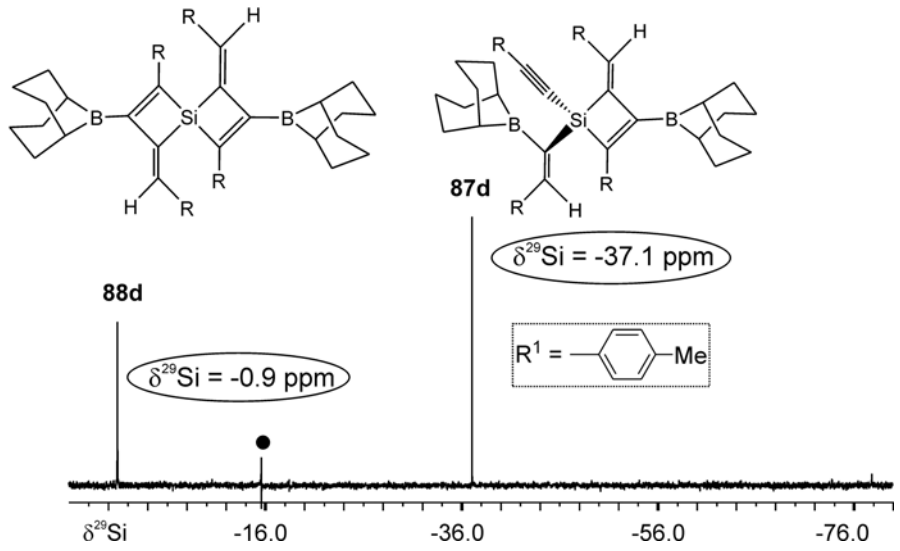


Figure 4.4. 59.6 MHz $^{29}Si\{^1H\}$ NMR spectra (refocused INEPT) showing the intermediate **87d** and final product **88d** (an artefact is marked by a filled circle).

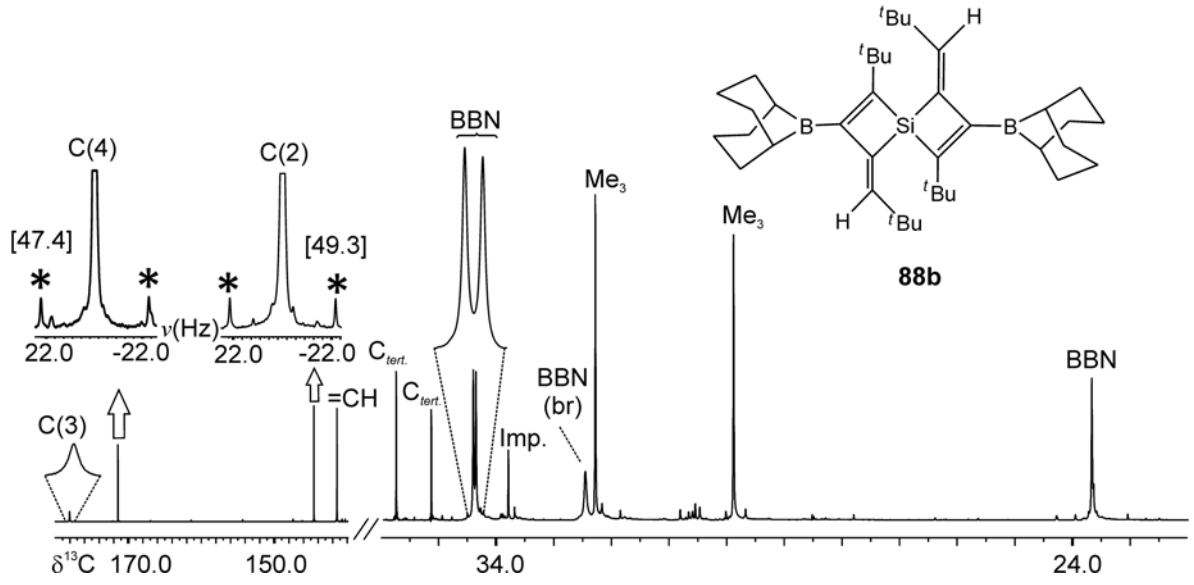


Figure 4.5. 100.5 MHz, $^{13}C\{^1H\}$ NMR spectra of the spirosilane **88b** (ca. 15 % (v/v) solution in C_6D_6). The ^{29}Si satellites for corresponding carbon signals in the expanded regions are marked by asterisks.

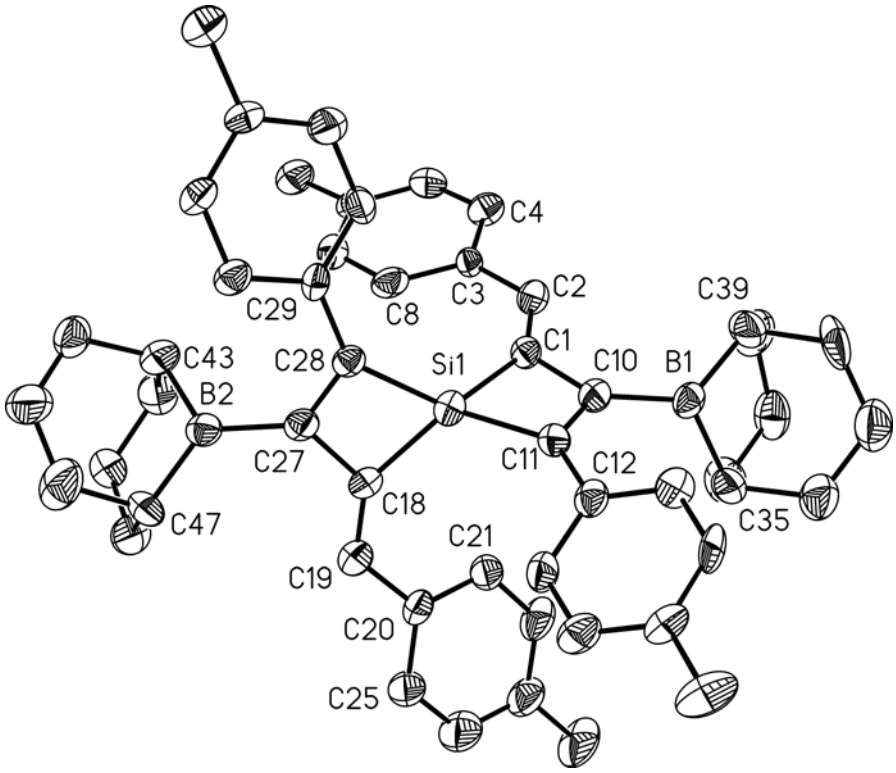


Figure 4.6. Molecular structure of the spirosilane **88d**. ORTEP plot (30 % probability level, hydrogen atoms are omitted for clarity) Selected bond lengths (pm) and bond angles (deg): C1-C2 134.5 (7), C1-C10 149.8 (10), C1-Si1 185.3 (7), C2-C3 144.1 (9), C10-C11 138.4 (8), C10-B1 158.8 (10), C11-C12 145.4 (10), C11-Si1 184.7 (8), C35-B1 158.2 (9), C39-B1 154.8 (9), C2-C1-C10 127.8 (7), C2-C1-Si1 144.0 (6), C10-C1-Si1 88.1 (4), C1-C2-C3 126.7 (7), C11-C10-C1 104.0 (6), C11-C10-B1 128.6 (7), C1-C10-B1 126.8 (6), C10-C11-C12 128.7 (8), C10-C11-Si1 91.9 (5), C12-C11-Si1 139.1 (7), C39-B1-C35 110.5 (6), C11-Si1-C1 75.8 (4).

*X-Ray structural analysis of **88d***

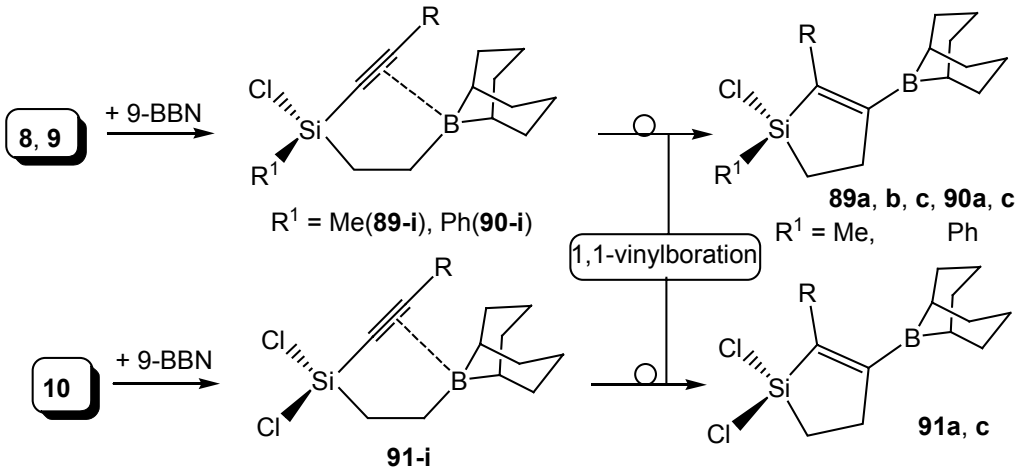
The molecular structure of **88d** is shown in Figure 4.6 together with selected bond lengths and angles, as the first example of structurally characterized compounds of this type of molecules. The data relevant to crystal structure determination are listed in Table 4.6. Although the crystals were non-meroedric twins, the structure could be determined without doubt to confirm the molecular connectivity and to obtain the relevant structural parameters. Intermolecular interactions appear to be negligible. The endocyclic bond angles are typically small (∠ C1Si1C11 = 75.9 and ∠ C18Si1C28 = 74.8 °) in contrast to the exocyclic bond angles (∠ C1Si1C18 130.8, ∠ C1Si1C28 124.9, ∠ C11Si1C18 125.2 and ∠ C11Si1C28 135.8). The endocyclic bond angles and all other angles and bond lengths in the ring systems

agree well with those previously reported for a related monocyclic silane.[111] Similarly the BC_2 planes of the 9-BBN groups are significantly twisted against the ring planes of the spiro-silane (∠ 56.1 and 55.3°) and are in agreement with the solution-state NMR data.

5. 1-SILACYCLOPENT-2-ENES

5.1. 1,2-Hydroboration of monoalkyn-1-yl(vinyl)silanes using 9-BBN as hydroborating reagent.

A number of groups on silicon atom such as, Ph, Me, H and Cl, discussed so far, have been introduced. The hydroboration of vinyl group is of great importance at least when 9-BBN is used as hydroborating reagent. It is well known that 9-BBN prefers terminal alkenes (-C=C bond) over -C≡C bond. The reactions take place at room temperature, provided that THF is used as the solvent. In this context, 9-BBN is an excellent reagent as it behaves differently when compared with other dialkylboranes. It definitely prefers vinyl -CH=CH_2 groups over -C≡C bonds.[124] In the case of monoalkyn-1-yl(vinyl)silanes **8 - 10**, it was found that 9-BBN preferably attacks the Si-vinyl group (> 95 % according to NMR spectra of reaction solutions, Figure 5.1), leading to respective short-lived intermediates **89-i** to **91-i**. These intermediates rearrange fast *via* intramolecular 1,1-vinylboration into 1-silacyclopent-2-enes **89** - **91**. This particular reaction sequence has already been found for analogous silanes[68,69] and the structures have been confirmed in solution as well as solid state. The silanes studied already, possess $SiMe_2$ and $SiPh_2$ units,[68,69] while in present work the interest was in Si-Cl function(s), and for this purpose alkyn-1-yl(vinyl)silanes bearing Si-Cl and Cl_2Si- units were studied. All the reactions were similar to the previously reported reactions.[68,69]



Scheme 5.1. Hydroboration of monoalkyn-1-yl(vinyl)silanes, formation of 1-silacyclopent-2-enes.

All the structures were confirmed by a consistent set of NMR data (Figure 5.1; ^{13}C NMR spectrum of **89a**) and molecular structure of **89c** was studied in solid state by X-ray diffraction. Both the solution state and the solid state structures are in close agreement with the proposed structures.

NMR spectroscopy

The proposed structures of heterocycles **89 - 91** in solution follow conclusively from the consistent set of NMR data (^{11}B, ^{13}C ^{29}Si) given in Table 5.1. The ^{13}C NMR spectra were recorded with a sufficient signal-to-noise ratio and almost all ^{29}Si satellites corresponding to $^{1}J(^{13}C,^{29}Si)$ and $^{2}J(^{13}C,^{29}Si)$ were observed for the silanes. The coupling constants provide a wealth of information on ^{13}C assignments. Furthermore the assignments were based on typical broad ^{13}C(B-C) NMR signals for boron-bonded ^{13}C nuclei. Based on their characteristic regions all the 1-silacyclopent-2-ene, ring carbons could be easily assigned, i. e. aliphatic and olefinic. The carbon C-2 and C-3 appear in olefinic region, carbon C-2, directly bonded to silicon can be identified from ^{29}Si satellites, and there is the typically broad ^{13}C(BC-3) NMR signal. The remaining two signals for ring carbons can be seen in the aliphatic region, ^{13}C(C-5) with ^{29}Si satellites for $^{1}J(^{13}C,^{29}Si)$ appears at lower frequency (δ = 12-13 ppm) than the ^{13}C(C-4) NMR signal ($\delta \approx$ 34 ppm). Similarly three signals (sometimes four when rotation is restricted) can be seen for the 9-BBN moiety.

The ^{29}Si NMR spectra are useful in the same way as ^{13}C, since the starting silanes and 1-silacyclopent-2-enes possess distinct silicon chemical shifts. This is very useful for monitoring the progress of the reactions. The ^{11}B NMR signals were observed in the range of δ 85 - 86 ppm, typical of three-coordinated exocyclic boron.[68 - 70,111] The solution state data are in agreement with the propose structure and the structures were confirmed in solid state by X-ray crystallography.

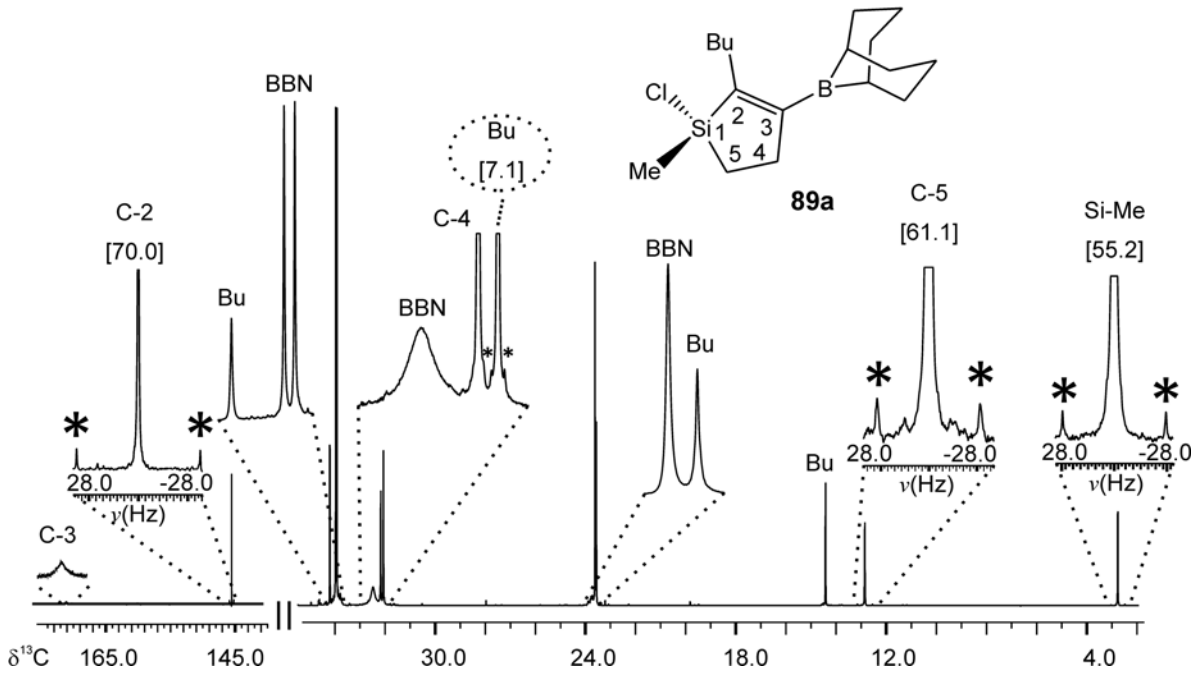


Figure 5.1. $^{13}C\{^{1}H\}$ NMR 100.4 MHz spectra with complete assignments of **89a**, expansions are shown for the ^{13}C NMR signals with ^{29}Si satellites for $^{1}J(^{13}C,^{29}Si)$ and $^{2}J(^{13}C,^{29}Si)$.

*X-ray structure analysis of **89c***

The molecular structure of **89c** is shown in Figure 5.2 together with selected bond lengths and angles. The related crystal data are listed in Table 5.2. The five-membered ring (Si1-C1-4) shows slight mean deviation of 83 pm from the mean plane. The phenyl group (C5 - C10) is twisted by 30° and CBC plane of 9-BBN is oriented by 122.2° to the five-membered ring. The geometry around the boron atom is trigonal planar, and additional interactions involving the boron atom were not observed. The geometry around the silicon atom is distorted tetrahedral with an expectedly small endocyclic angle ∠ C1-Si1-C4 = 94.9°. The C2-C3 bond (153.1 pm) and C3-C4 bond (154.0 pm) are slightly elongated due to hyperconjugation where the empty boron p_z orbital and C-C σ bonds are involved. All other bond lengths and angles are comparable with the reported structures.[68,69]

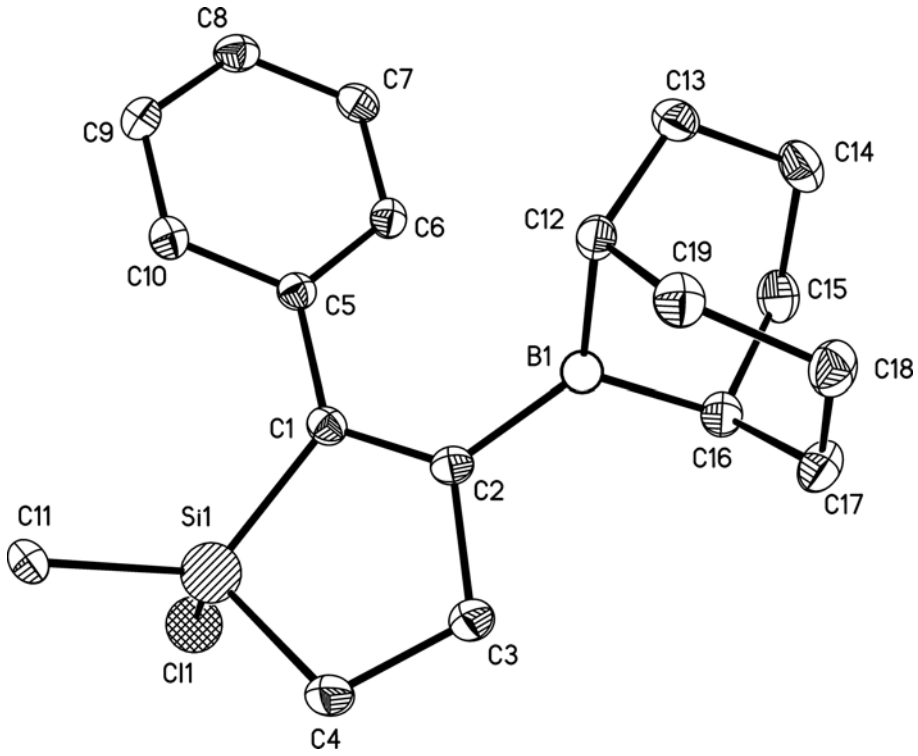


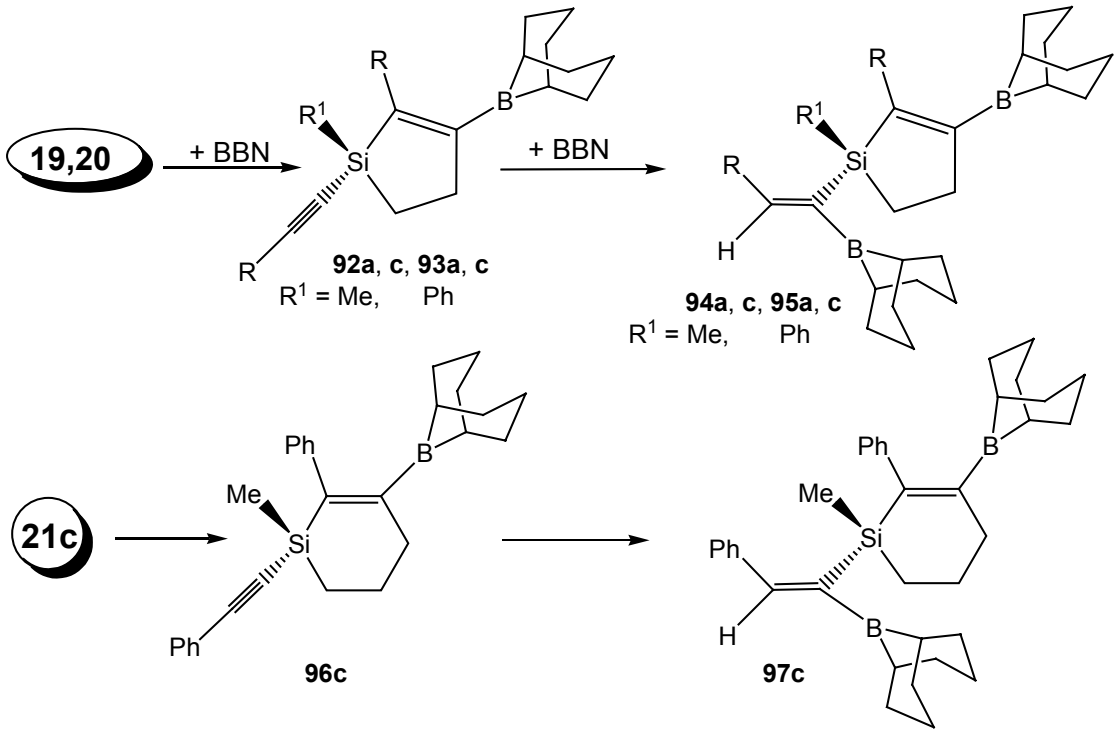
Figure 5.2. Molecular structure of 3-(9-borabicyclo[3.3.1]nonyl)-1-chloro-1-methyl-2-phenyl-1-silacyclopent-2-ene, **89c**, ORTEP plot (50 % probability, hydrogen atoms are omitted for clarity). Selected bond lengths (pm) and angles (deg): C1-C2 135.7 (2), C1-C5 147.5 (2), C1-Si1 185.5 (15), C2-C3 153.1 (2), C2-B1 156.2 (2), C3-C4 154.0 (2), C4-Si1 185.2 (17), C11-Si1 186.4 (17), Si1-Cl1 208.4 (6), C2-C1-Si1 109.3 (11), C1-C2-C3 116.8 (13), C3-C4-Si1 104.4 (11), C4-Si1-C1 94.9 (7), C1-Si1-C11 120.1 (7), C1-Si1-Cl1 109.5 (5), C4-Si1-Cl1 109.9 (6), C11-Si1-Cl1 105.7 (6), C4-Si1-C11 116.4 (8), C5-C1-Si1 126.7 (11), C2-C1-C5 123.9 (14), C12-B1-C16 111.4 (13), C2-B1-C16 123.6 (14), C12-B1-C2 123.3 (14).

5.2. 1,2-Hydroboration of dialkyn-1-yl(vinyl)silanes using 9-BBN as hydroborating reagent

The silanes **19** and **20** were obtained as side products accompanied by silanes **8** and **9** (Scheme 2.4). These silanes were separated by conventional fractional distillation. The pure samples were then treated with 9-BBN in THF. The reaction (combination of 1,2-hydroboration and 1,1-vinylboration) leads to 1-silacyclopent-2-enes **92** and **93** (Scheme 5.2). Hence, these silanes possess further functional groups (Si-C=C and Si-C≡C-) which can react with 9-BBN to afford the products, 1-(alkenyl)-1-silacyclopent-2-enes (**94**, **95**). The reactions were carried out at room temperature with one equivalent of 9-BBN and mainly products like **92** and **93** were

obtained while further one equivalent of the same hydroborating reagent led to products **94** and **95** at relatively high temperature (80-100 °C). It was observed that once the boryl group (9-BBN) is introduced into the molecule, the system undergoes 1,1-vinylboration under the same reaction conditions. This whole process comes to an end in 1-2 h. in the next step, the remaining one equivalent of 9-BBN reacts with Si-C≡C- function at high temperature of 80 - 100 °C, to afford the final products. All the compounds obtained in this series were oily liquids and were characterized by NMR spectroscopy (Figure 5.3).

The silane **21c** was treated with 9-BBN in a similar way as **19** and **20**. It was proved once again that 9-BBN prefers the terminal -C=C bond (allyl group) over the Si-C≡C- unit, and the reaction affords 1-(alkyn-1-yl)-1-silacyclohex-2-ene i.e. **96c**. In the next step, the remaining amount of 9-BBN (added in twofold excess) reacts at 80 - 100 °C to afford quantitatively 1-silacyclohex-2-ene derivative, **97c**. Compounds **96c** and **97c** are air and moisture sensitive oily products, soluble in benzene and were studied by NMR spectroscopy.



Scheme 5.2. Combination of 1,2-hydroboration and 1,1-vinylboration, formation of 1-silacyclopent-2-ene and 1-silacyclohex-2-ene derivatives.

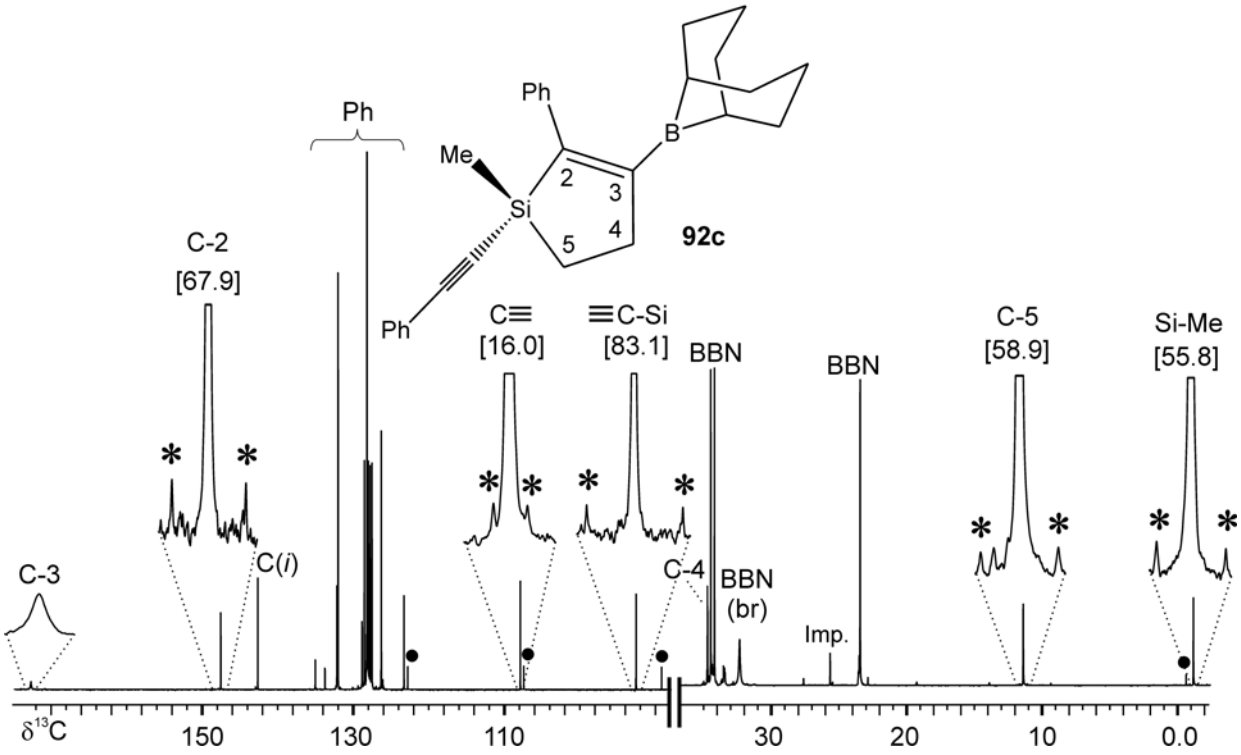


Figure 5.3. 100.5 MHz $^{13}C\{^1H\}$ spectrum of 3-(9-borabicyclo[3.3.1]nonyl)-1-methyl-1-phenylethynyl-2-phenyl-1-silacyclopent-2-ene **92c**, 10 - 15 % solution in C_6D_6. The reaction mixture containing starting silane **19c**, marked by filled circles. Note the broad signals, typical of the boron-bonded carbon atoms.[97,98] ^{29}Si satellites marked by asterisks correspond to $^1J(^{13}C,^{29}Si)$.

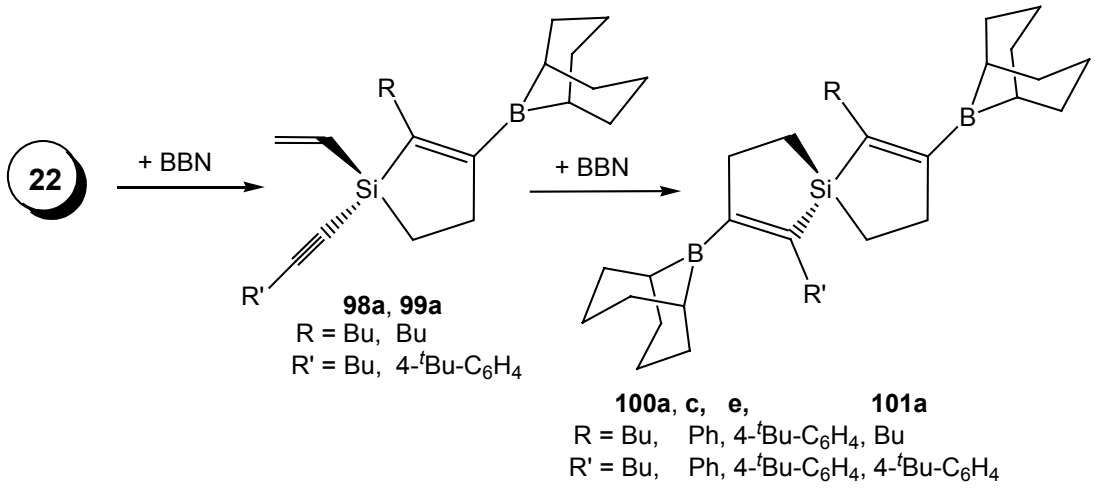
NMR spectroscopic results

The NMR spectroscopic data (^{11}B, ^{13}C, ^{29}Si and ^1H) of 1-silacyclopent-2-ene derivatives (**92** - **95**) are given in Table 5.3, Table 5.4 and Experimental part, respectively. The data set is consistent with that obtained for simple 1-silacyclopent-2-enes (Table 5.1). In ^{13}C NMR spectra, all the ring carbons can be assigned easily as discussed for compounds **89 - 91**. The signals corresponding to the basic functional groups Si-(B)C=C- and Si-C≡C- can also be assigned unambiguously. The former group exhibits a broad (C-B) and a sharp (=CH) signals in the olefinic region and were assigned without performing special measurements. In the latter case (Si-C≡C-) both the ^{13}C NMR signals are accompanied by the typical ^{29}Si satellites. The ^{29}Si NMR spectra are useful in monitoring the progress of the reactions and to detect various compounds in the reaction mixtures, as they possess distinct ^{29}Si chemical shifts, for example, δ -6.0 ppm (**92a**) and δ 7.3 ppm (**94a**). In ^1H NMR spectra, the signals appear in the aromatic region for =CH and is particularly informative in case

of **94** and **95**. Very less information can be obtained from ^{11}B NMR spectra as they cover a narrow range (δ = 84 - 86 ppm) and also signals for other compounds in the mixture are not resolved. However, broad signals appeared for more than one component of the mixture (*e.g.* **92a** and **94a**, δ = 84.4 ppm).

The structural assignments of 1-silacyclohex-2-ene derivatives (**96c**, **97c**) were similar to those of 1-silacyclopent-2-enes. All the ring carbons (Table 5.5) are clearly identified by their characteristic ^{13}C chemical shifts. The ^{13}C(C-2) (sharp with ^{29}Si satellites) and the ^{13}C(BC-3) (broad) signals in the olefinic region can be assigned unambiguously. In the aliphatic region the signals belong to C-4, C-5 and C-6 can easily be distinguished from those of the 9-BBN group.

5.3. 1,2-Hydroboration of dialkyn-1-yl(divinyl)silanes, formation of spirosilanes



Scheme 5.3. Formation of spirosilanes by the reaction of dialkyn-1-yl(divinyl)silanes **22** with 9-BBN.

Pure samples of silanes **22** and **23** were treated with 9-BBN at room temperature as discussed for the above mentioned systems in THF. The aim of the reactions was to achieve spirosilanes and to study them in solution by NMR spectroscopy and in solid state by X-ray crystallography, if possible. One equivalent of 9-BBN affords 1-silacyclopent-2-enes **98a** and **99a**. Which bears still reactive functional groups (Si-vinyl and Si-C≡C-) and can react with the same amount (one equivalent) of 9-BBN to afford the desired spirosilanes **100** and **101**. The method of combining of 1,2-hydroboration and 1,1-vinylboration for the syntheses of spirosilanes (Scheme 5.3) is particularly important as it involves only one purification

step in the beginning and the reactions take place at ambient temperature (ca. 25 °C). All the final products were oily liquids, waxy solid (**100e**) or crystalline (**100c**) materials. Single crystals suitable for X-ray structural analysis of **100c** were obtained and the molecular structure was determined.

NMR spectroscopic results

The NMR data (^{11}B, ^{13}C, ^{29}Si) corresponding to intermediates **98a** and **99a** and spirosilanes (**100** and **101**) are listed in Table 5.8 and Table 5.7, respectively. The ^{1}H NMR data sets are given in Experimental section. The data obtained are similar to simple 1-silacyclopent-2-enes **89 - 95**. In ^{13}C NMR spectra, signals belonging to all the ring carbons are readily assigned based on ^{29}Si satellites for $J(^{13}C,^{29}Si)$ (Figure 5.5). The chemical shifts of all other ^{13}C nuclei are within the expected range. In the similar way ^{1}H spectra contain multiplets for H_2C-CH_2 protons in the aliphatic region and were not assigned to intermediates **98a** and **99a** formed as minor components in mixtures. The ^{29}Si NMR spectra were used as a powerful tool for the determination of various intermediates present in the reaction mixture (Figure 5.4).

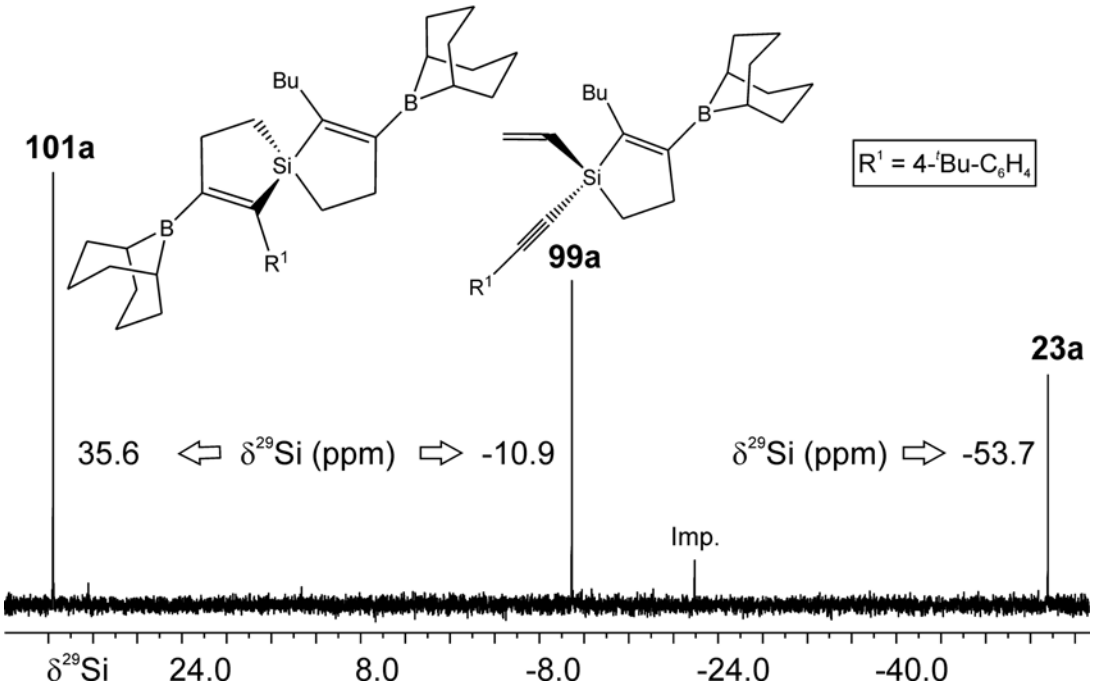


Figure 5.4. ^{29}Si{^{1}H} NMR 59.6 MHz spectra of the reaction mixture containing starting silane **23a**, intermediate **99a** and spirosilane **101a**. All three compounds possess characteristic ^{29}Si chemical shift and can readily be identified.

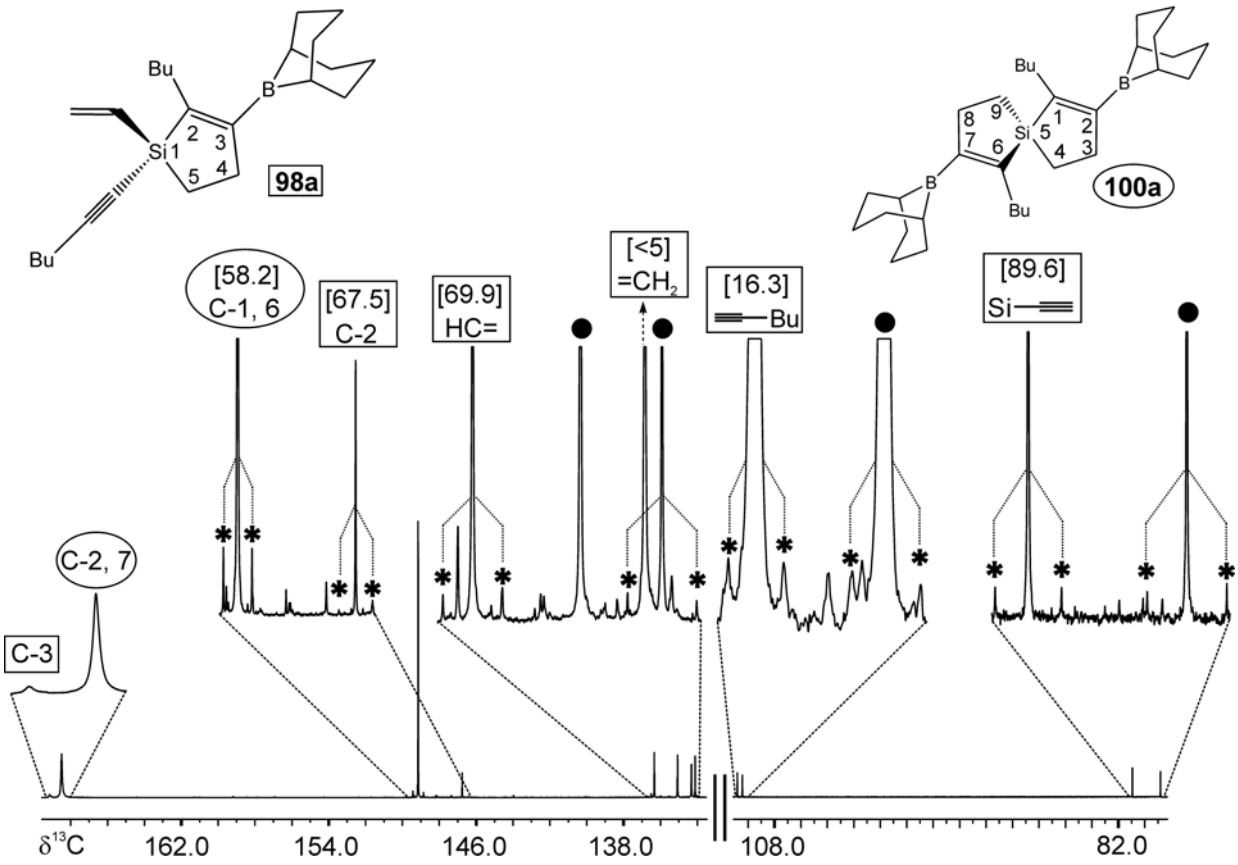


Figure 5.5. Part of 100.5 MHz $^{13}C\{^{1}H\}$ NMR spectra in C_6D_6, of the reaction mixture, carried out at room temperature, showing three compounds, starting materials **22a**, intermediate, **98a** and final product **100a**.

*X-ray structure analysis of spirosilane **100c***

Molecular structure of 2,7-bis[(9-borabicyclo[3.3.1]nonyl)]-1,6-diphenyl-5-silaspiro[4.4]nona-1,6-diene **100c** is shown in Figure 5.6 together with selected bond lengths and angles. The data regarding structure refinements and solutions are listed in Table 5.8. All the bond lengths and angles are comparable with those listed for simple 1-silacyclopent-2-ene **89c.** All atoms of the five-membered rings (SiC4) are in the same plane with a slight deviation Si1-(C1-4) = 9.3 pm and Si1-(C11-14) = 1.8 pm). Both the SiC4 planes are almost perpendicular to each other (twisted by 84.9°). The CBC planes of 9-BBN on both rings are twisted by 52.2° (C21-B1-C25) and 55.4° (C29-B2-C33), the geometry around the boron atoms is trigonal planar. The molecule has two expectedly small endocyclic angles (∠ C1-Si1-C4 = 93.0° and ∠ C11-Si1-C14 = 93.4°) in contrast to exocyclic angles (∠ C1-Si1-C14 = 121.3°, ∠ C1-Si1-C11 = 111.5°, ∠ C4-Si1-C14 = 119.3° and ∠ C4-Si1-C11 = 120.5°).

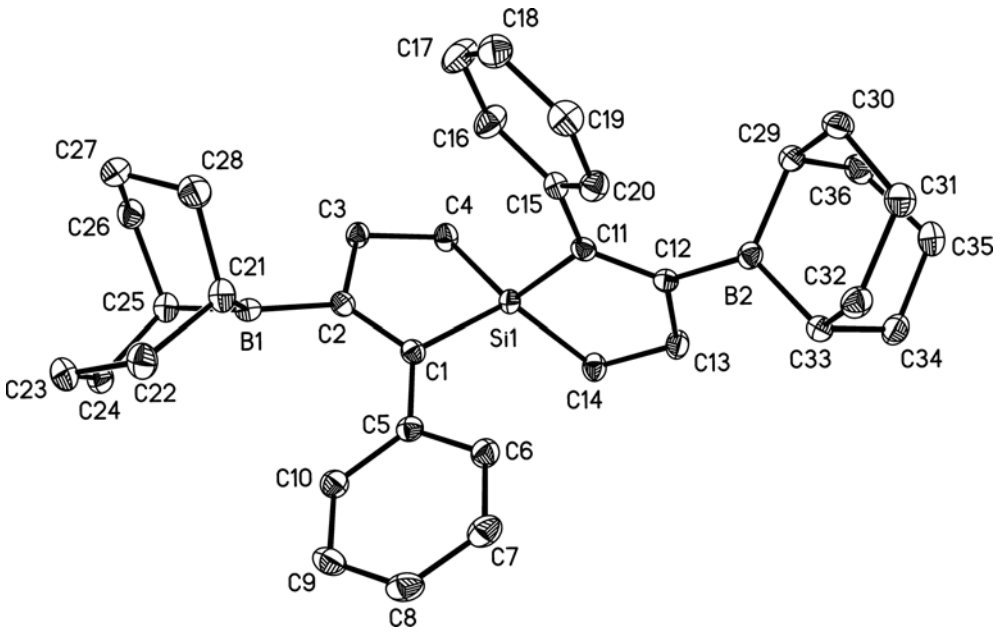


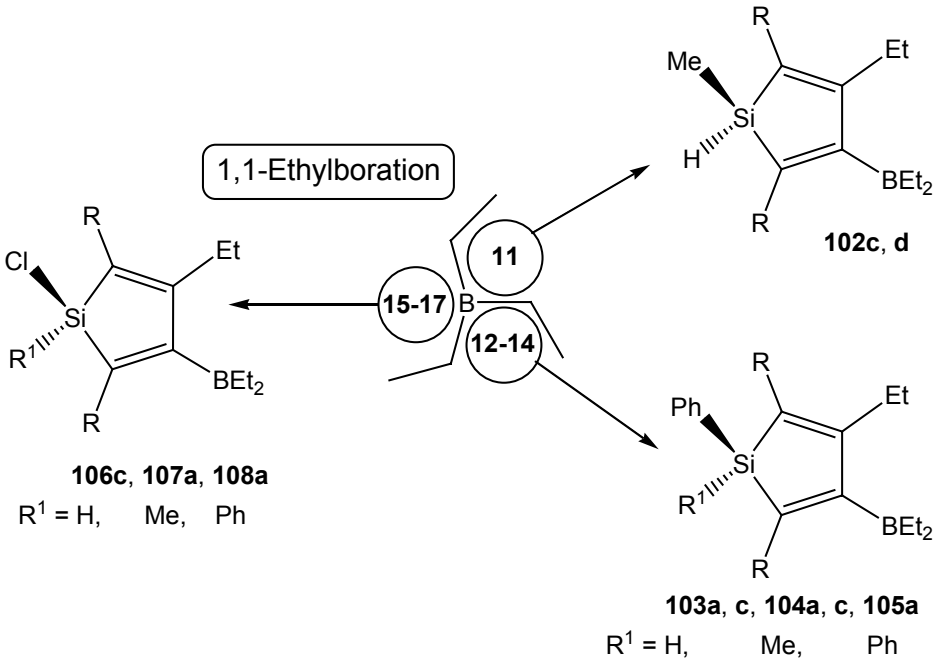
Figure 5.6. Molecular structure of 2,7-bis[9-(9-borabicyclo[3.3.1]nonyl)]-1,6-diphenyl-5-silaspiro[4.4]nona-1,6-diene, **100c**. ORTEP plot (40 % probability level, hydrogen atoms are omitted for clarity). Selected bond lengths (pm) and angles (deg.): C1-C2 135.8 (19), C1-C5 147.2 (19), C1-Si1 186.7 (14), C2-C3 152.6 (19), C2-B1 155.8 (2), C3-C4 154.2 (19), C4-Si1 187.7 (14), C21-B1 157.0 (2), C25-B1 157.1 (2), C2-C1-C5 123.0 (12), C2-C1-Si1 110.0 (10), C1-C2-C3 116.6 (12), C2-C3-C4 111.7 (11), C3-C4-Si1 104.9 (9), C1-Si1-C11 111.5 (6), C1-Si1-C14 121.3 (7), C1-Si1-C4 93.0 (6), C11-Si1-C4 120.5 (6), C14-Si1-C4 119.3 (6), C21-B1-C25 111.4 (12), C2-B1-C21 122.9 (12).

6. 1,1-ORGANOBORATION

6.1. 1,1-Organoboration of dialkyn-1-ylsilanes

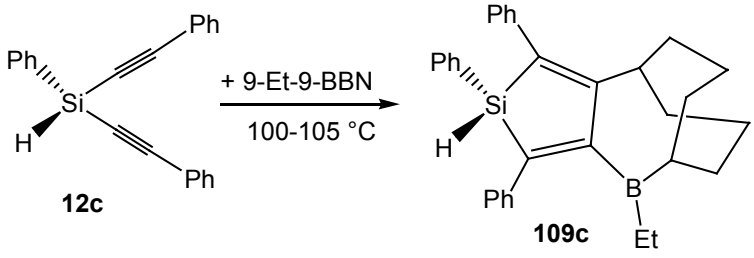
The alkyn-1-ylsilanes bearing at least two Si-C≡C- functions react with BEt_3 under harsh reaction conditions (80 – 120 °C, for several days) to afford siloles (1-silapenta-2,4-dienes). Siloles present an expanding field in chemistry as they can be used in modern electronics. Various methods are available for the preparation of siloles,[125] 1,1-organoboration is an efficient way to prepare siloles. Starting silanes with two or more than two Si-C≡C- functional groups were obtained as the side products (discussed in Chapter 2) and were treated with BEt_3 to afford siloles. Several types of siloles bearing different substituents on the silicon atom as well as on all the silole ring positions, were synthesized using new dialkyn-1-ylsilanes and trialkyn-1-ylsilanes. Siloles synthesized *via* 1,1-organoboration have been extensively studied.[29,56] It is already mentioned that the silanes **11 - 17** were obtained as side products accompanying the monoalkyn-1-ylsilanes (Scheme 2.1 and Scheme 2.2). The main objective of these reactions was to utilize the side products for useful purposes, like formation of siloles and to study their further reactions (*e. g.* protodeborylation of siloles, Chapter 7). Thus, the silanes **11 - 17** were treated with an excess amount of BEt_3 at elevated temperature, heating lasted from few hours to several days. The reactions were monitored as usual by ^{29}Si NMR spectroscopy. After removal of all volatile materials, the products were charatcterized and used without further purification.

The dialkyn-1-yl(chloro)silanes **15 - 17** were treated in the same way as silanes **11 - 14** with BEt_3. It was observed that the Si-Cl function not only reduces the reactivity of Si-C≡ bond but also diverts the reactivity of these silanes to undergo 1,2-hydroboration on treatment with BEt_3. It is already discussed (Chapter 4) that dialkyn-1-ylsilanes bearing one Si-Cl function are border line compounds, since some of them afforded 1-silacyclobutenes while others gave the expected siloles. The silanes bearing -C≡C-Ph functions followed the new route (1,2-hydroboration to afford 1-silacyclobutenes) where BEt_3 acts as hydroborating reagent (Scheme 4.2). In contrast, the silanes bearing -C≡C-Bu group reacted *via* the expected route and afforded siloles (Scheme 6.1). Siloles were achieved in almost quantitative yield as oily liquids and were studied by multinuclear NMR spectroscopy. The reaction mechanism is already discussed in Chapter 1 (Scheme 1.3).



Scheme 6.1. Reaction of different types of dialkyn-1-ylsilanes with BEt_3 to afford corresponding siloles.

The silane **12c** was treated with 9-ethyl-9-borabicyclo[3.3.1]nonane observing almost identical harsh reaction conditions (100 - 105 °C, 3 d) as described for other siloles. The reactions afforded the silole **109c** as the major product which could be crystallized. Although the quality of crystals was not perfect owing to their small size, the crystal structure could be solved unambiguously. The broad ^{29}Si NMR signal, some ^{13}C (*ipso* carbons of Ph) and ^{1}H(Si-H) NMR signals indicate dynamic behaviour of the molecule at least in solution. The comparison of solution state data (NMR, Table 6.1) and solid state data (X-ray diffractions) reveals that the main features of the molecular structure of the silole are retained in both phases.



Scheme 6.2. Reaction of diphenylethynyl(phenyl)silane with 9-ethyl-9-borabicyclo-[3.3.1]nonane.

NMR spectroscopic studies

The siloles **102 - 109** are brownish, moisture and oxygen sensitive oily compounds. They are soluble in benzene and could be studied by NMR spectroscopy (^{11}B, ^{13}C and ^{29}Si) in solution (Table 6.1). The reactions were constantly monitored by ^{29}Si NMR spectroscopy. The starting materials and final products (siloles) possess distinct ^{29}Si chemical shifts and therefore, ^{29}Si NMR was helpful in monitoring the progress of the reactions. The ^{29}Si resonance signals for dialkyn-1-ylsilanes were shifted towards high frequency by 45 - 51 ppm, which clearly indicates the formation of the siloles. If the ^{29}Si NMR spectra are measured for relatively long time in order to get good signal-to-noise ratio, the ^{13}C satellite signals appear corresponding to $J(^{13}C,^{29}Si)$ coupling constants (Figure 6.1). The coupling constants obtained from ^{13}C NMR spectra were confirmed by ^{13}C satellites in respective ^{29}Si NMR spectra. In ^{13}C NMR spectra the ring carbons are easy to assign based on $J(^{13}C,^{29}Si)$ and the broad signal for the carbon bonded to BEt_2 group. An overview of the data shown in Table 6.1 shows that all the siloles must have very similar structures. The ^{11}B chemical shifts are in the expected range (δ 86.0 - 87.0 ppm), typical of exocyclic three-coordinated boron atoms. In ^{1}H NMR spectra (Experimental part), the appearance of new signals corresponding to Et and BEt_2 groups could be observed when the reaction becomes complete.

Since the siloles bearing Si-Cl function (**106 - 108**) were impure due to some side reactions, it was not possible to assign all the signals. The reaction products can be proposed from ^{29}Si spectra and part of ^{13}C NMR spectra (silole ring carbons in olefinic region). Similarly, in the ^{1}H NMR spectra of siloles **107** and **108** all the protons (Et, BEt_2 and Bu) were observed as overlapping multiplets and could not be assigned.

*X-ray structure analysis of silole **109c***

The molecular structure of silole **109c** is shown in Figure 6.2 together with selected parmeters. The data pertinent to crystal structure determination are listed in Table 6.2. The reactivity of 9-ethyl-9-borabicyclo[3.3.1]nonane with dialkyn-1-ylsilanes is similar to that of dialkyn-1-ylstannanes.[126] The geometry around silicon atom is distorted tetrahedral with a small endocyclic angle of 92.3°. The value of this particular angle fall in the range of 90.5 - 97°[127] and a rather large value has been reported for 1,1-dibromosilole.[58] Substitution of groups at 2 and 5 position by an

electronegative atom results in a decrease of the C-Si-C endocyclic angle.[127] All atoms of the silole ring (principle plane) are almost in the same plane with a slight mean deviation of 2.6 pm. The silole ring exhibits both C=C as well as C-C bond characters within the experimental error.[128] The geometry around the boron atom is trigonal planar, all atoms (CBCC) are exactly in the same plane and C7-B1-C20 plane is twisted by an angle of 122.0° against the silole plane. The substituents (Ph) on C1 and C13 are twisted by 119.5° and 25.7°, respectively, while the Si-Ph group makes an angle of 92.9° with the principle plane. All other bond lengths and angles are within expected range. Intermolecular or intramolecular interactions were not considerable.

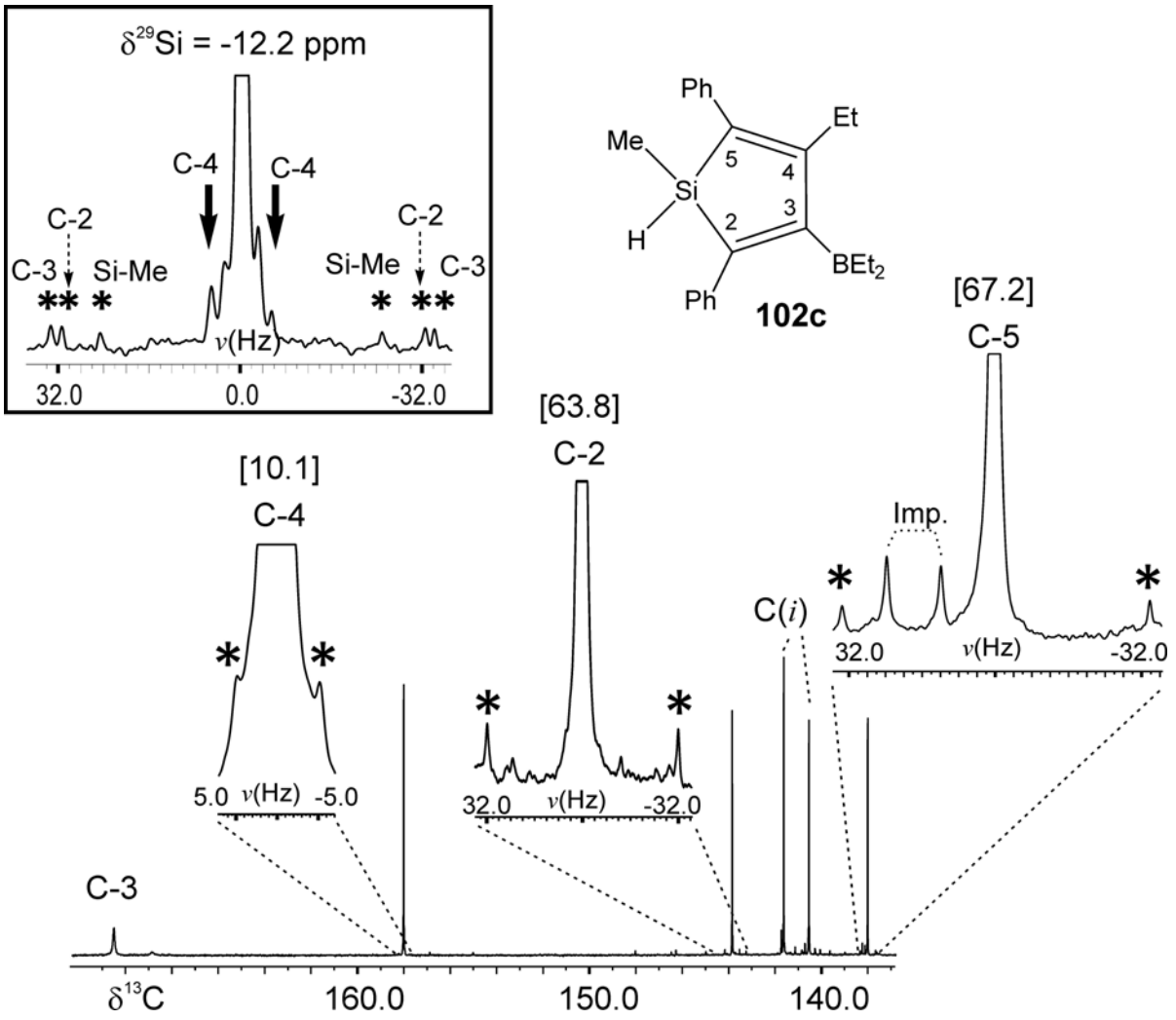


Figure 6.1. 59.6 MHz $^{29}Si\{^{1}H\}$ (upper inserted, expansion of parent signal) and part of 100.5 MHz $^{13}C\{1H\}$ NMR spectra of **102c**. Coupling constants $^{1}J(^{13}C,^{29}Si)$ and $^{2}J(^{13}C,^{29}Si)$ are shown in expansions. The ^{13}C(BC-3) NMR signal is typically broad.

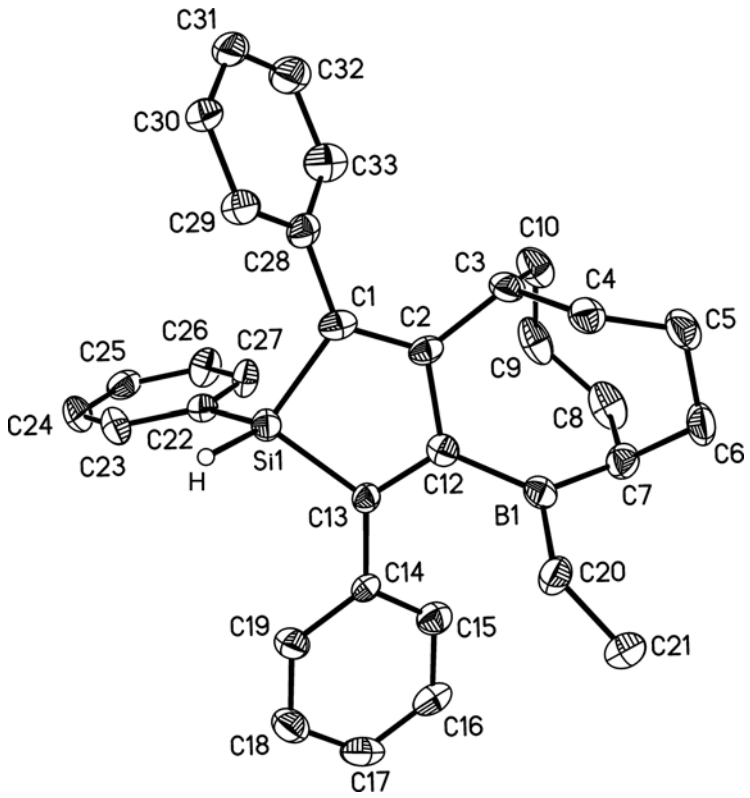
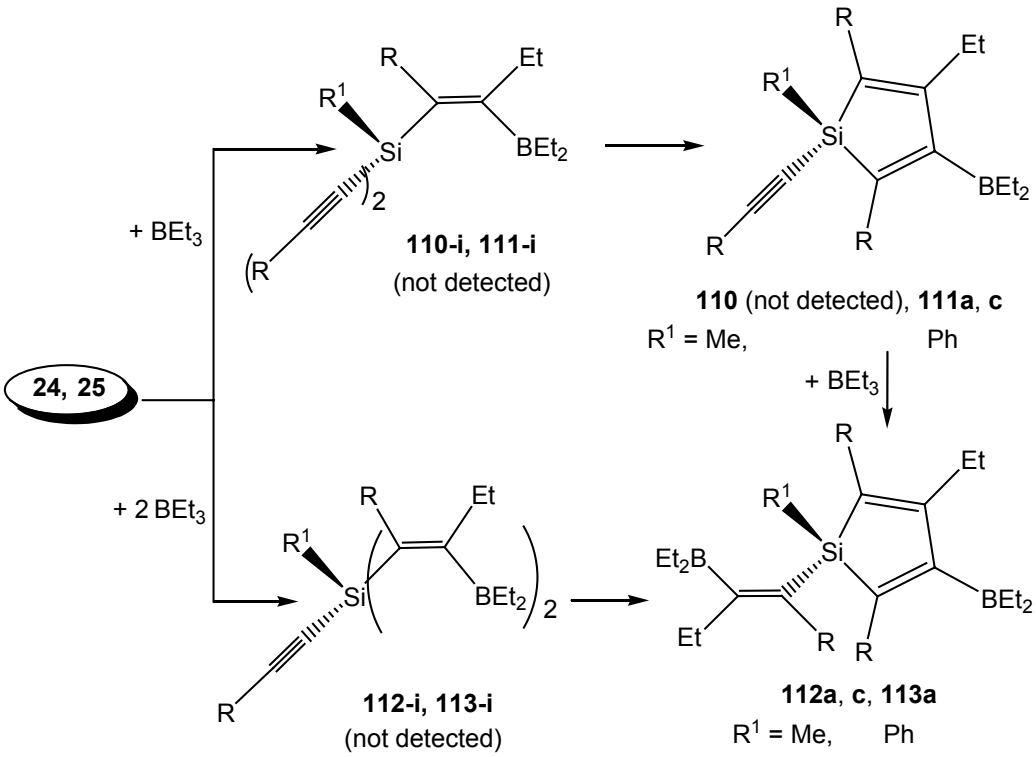


Figure 6.2. Molecular structure of silole **109c** (ORTEP plot, 40 % probability, hydrogen atoms except Si-H are omitted for clarity) Selected bond lengths (pm) and angles (deg): C1-C2 135.1 (6), C2-C12 151.6 (6), C12-C13 137.3 (6), C13-Si1 186.1 (4), C1-Si1 185.4 (4), C22-Si1 186.7 (4), C1-C28 148.0 (6), C2-C3 151.0 (6), C13-C14 147.1 (6), C7-B1 157.7 (7), B1-C12 157.0 (7), B1-C20 158.3 (6), C2-C1-Si1 108.3 (3), C1-C2-C12 116.4 (4), C13-C12-C2 113.9 (4), C12-C13-Si1 108.6 (3), C1-Si1-C13 92.3 (2), C1-Si1-C22 112.64 (17), C28-C1-Si1 125.2 (3), C12-B1-C7 127.0 (4), C12-B1-C20 115.1 (4), C7-B1-C20 117.8 (4).

6.2. Syntheses of 1-alkenyl- and 1-alkyn-1-yl-substituted siloles.

The siloles bearing Si-C=C(B) or Si-C≡C- groups were considered as the next series of compounds to be obtained *via* the same process of 1,1-organoboration. The silanes **24** and **25** were reacted with BEt_3. The reaction mixtures were heated to 120 °C for several days. The reactions proceed through intermediates **110-i**, **111-i** (not detected) when one equivalent of BEt_3 react with the respective silane and **112-i**, **113-i** (not detected) when two equivalents of BEt_3 (present in excess) react with the corresponding silane. The nature of organyl groups Si-C≡C-R as well as Si-R influence the second 1,1-ethylboration. Silanes, Me-Si(C≡C-R)$_3$ (R = Bu, Ph) **24a**, and **24c** afforded mainly the silole **112a** and **112c** (Scheme 6.3). Attempts were

made to achieve data for silole **110a** and **110c**, however, in vain. It indicates that siloles **110a** and **110c** are least stable and react immediately with BEt_3 to afford **112a** and **112c** at elevated temperature. Such products (siloles) are the result of threefold successive 1,1-organoboration reactions. The first intermolecular 1,1-ethylboration is followed by intramolecular 1,1-vinylboration and once a silole ring has been formed, the third intermolecular 1,1-ethylboration of Si-C≡C- function affords the final siloles **112a** and **112c**. In the case of silane **24**, there is no chance to detect **110a** and **110c**, immediate precursors of **112a** and **112c**, in the reaction mixture. In contrast, the silane Ph-Si(C≡C-R)$_3$ (R = Bu, Ph) **25a** and **25c** afforded the principle products, siloles **111a** and **111c**. They were obtained in relatively high quantity. Some other minor unknown products as a result of side reactions were also observed including **113** (δ^{29}Si = 5.6 ppm, **113a**). The presence of the side products make the complete assignments of NMR signals more difficult.



Scheme 6.3. Formation of siloles with exocyclic Si-C=C(B) and Si-C≡C- functional groups.

NMR spectroscopic results

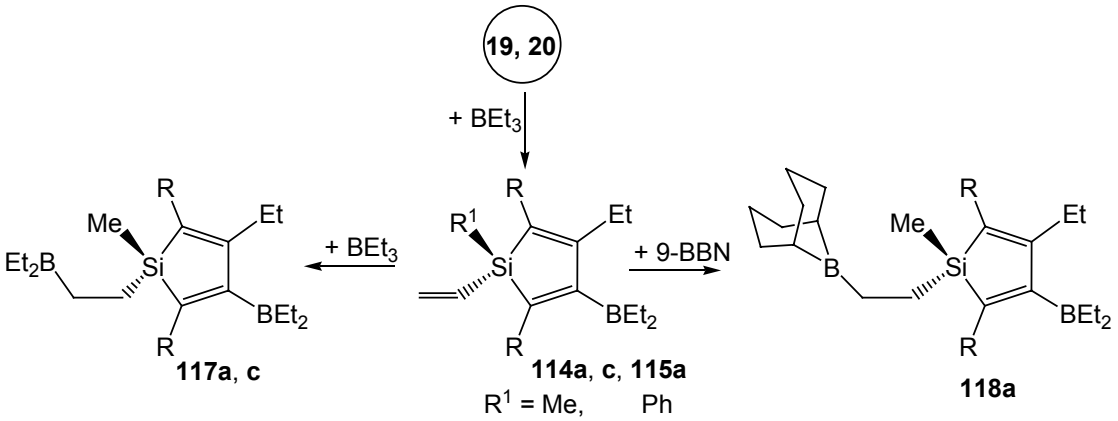
The NMR data (^{11}B, ^{13}C and ^{29}Si) of siloles bearing Si-C=C(B) (**111a** and **111c**) and Si-C≡C- functional groups (**112**) are listed in Table 6.3. Chemical shifts of all

carbons of the five-membered silole ring can be assigned as discussed for siloles **102 - 109**. In ^{13}C spectra the siloles **111 - 113** are well distinguishable. Reaction products of silanes **24** were identified as silole **112**. They possess an exocyclic Si-C=C(BEt_2) group, the carbons of Si-C=C(B) group can easily be identified from their characteristic properties, a broad ^{13}C(=C(B)) and a sharp ^{13}C(Si-C=) signal. The latter is always accompanied by ^{29}Si satellites corresponding to $^1J(^{13}C,^{29}Si)$ (≈ 67 Hz). In contrast, the reactions of silanes **25a** and **25c** with BEt_3 were not very clean, since a number of unknown side reactions take place. The desired products, siloles **113a** and **113c** were identified in the mixture (ca. 60 % from NMR data). The presence of Si-C≡C- functional group in siloles is readily apparent from ^{29}Si satellites for ^{13}C(C≡C) NMR signals. Assignments of signals for the five-membered silole ring carbons were straightforward as discussed for the aforementioned siloles (**102 - 109**).

6.3. 1,1-Ethylboration of dialkyn-1-yl(vinyl)silanes and dialkyn-1-yl(allyl)silanes

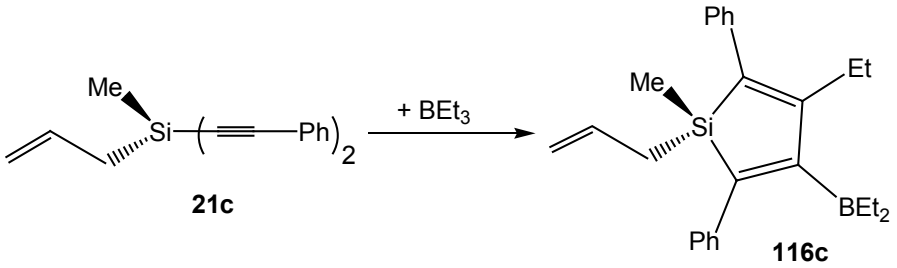
Reactions of a number of silanes bearing various functional groups on the silicon atom (H, Cl, -C≡C-, -C=C-) with BEt_3 were explored (siloles **102 - 112**) in this work. In some cases the reactivity of BEt_3 was surprising *e.g.,* Me(Cl)Si(C≡C-Ph)$_2$ **16c** and Ph(Cl)Si(C≡C-Ph)$_2$ **17c** follow 1,2-hydroboration to afford 1-silacyclobutenes (**69 - 72**, Chapter 4) instead of 1,1-ethylboration. In other cases the reactions were straightforward and siloles (expected products) were obtained. Having a variety of functional groups, it was of interest to know whether Si-vinyl or Si-C≡C- functional group, present in the same molecule, is more reactive towards organoboration? The reactions reminded of the previous findings (Scheme 3.8) that Si-C≡C- is more reactive than the Si-vinyl bond (Figure 6.3). The reactions afforded siloles **114** and **115** as major products. The siloles **114a** and **114c** were left for long time (ca. 20 d) in contact with excess of BEt_3 at high temperature (100 - 120 °C) to afford 1-(2-diethylboranylethyl)siloles **117a** and **117c**. Further reactions of BEt_3 with siloles bearing a Si-vinyl group were too slow as compared to the silole formation. Also it was detected that 1,2-hydroboration instead of 1,1-ethylboration had occurred. This phenomenon was confirmed by treating the siloles **114a** and **114c** with well known hydroborating reagent 9-BBN at room temperature to get siloles **118a** and **118c** (Scheme 6.4). The NMR data collected were compared with the data achieved for siloles **117a** and **117c**. The data (mainly ^{13}C and ^{29}Si) obtained for **118a** and **118c** show very close resemblances with the data already in hand for siloles **117**. Based

on these facts it was concluded that 1,2-hydroboration of the exocyclic Si-C=C unit is preferred over 1,1-ethylboration.



Scheme 6.4. Hydroboration of vinyl-substituted siloles using BEt_3 and 9-BBN in parallel reactions.

The dialkyn-1-yl(allyl)silane **21c** was treated with BEt_3 under the same reaction conditions. The aim of this reaction was to find out whether 1,1-ethylboration of the Si-C≡C- bond or Si-allyl bond is preferred. The same phenomenon of silole formation as for **114** and **115** was observed. The allyl group remained untouched leading to clean formation of 1-(allyl)silole **116c** (Scheme 6.5).



Scheme 6.5. Formation of allyl-substituted siloles *via* 1,1-ethylboration.

NMR spectroscopic data

The NMR data (^{11}B, ^{13}C and ^{29}Si) of siloles **114** - **118** are collected in Table 6.4 and ^{1}H NMR data are listed in Experimental part. The data sets for the five-membered silole ring are consistent with the proposed structures. The ring ^{13}C NMR signals were assigned as discussed for the aformentioned siloles (**102 - 112**). New groups on silicon atom (vinyl and allyl) give self explainatory NMR data sets. The two carbons of Si-vinyl group, =CH and H_2C= can be observed in olefinic region of ^{13}C NMR spectra. For identification of the Si-CH=CH_2 group, a wealth of information can

be obtained from ^{1}H NMR spectra. Protons of vinyl groups (H_2C=CH) in most of the cases exhibit different chemical shifts. These protons can be perfectly assigned on the basis of $J(^{1}H,^{1}H)$ spin-spin coupling constants. On further reaction with BEt_3 or 9-BBN these signals disappear and new signals in the aliphatic region arise, representing new, siloles, **117** and **118**, respectively. The ^{29}Si NMR spectra provide further information about progress of the reaction and different products in the reaction mixture. This tool was used throughout for monitoring the progress of the reactions.

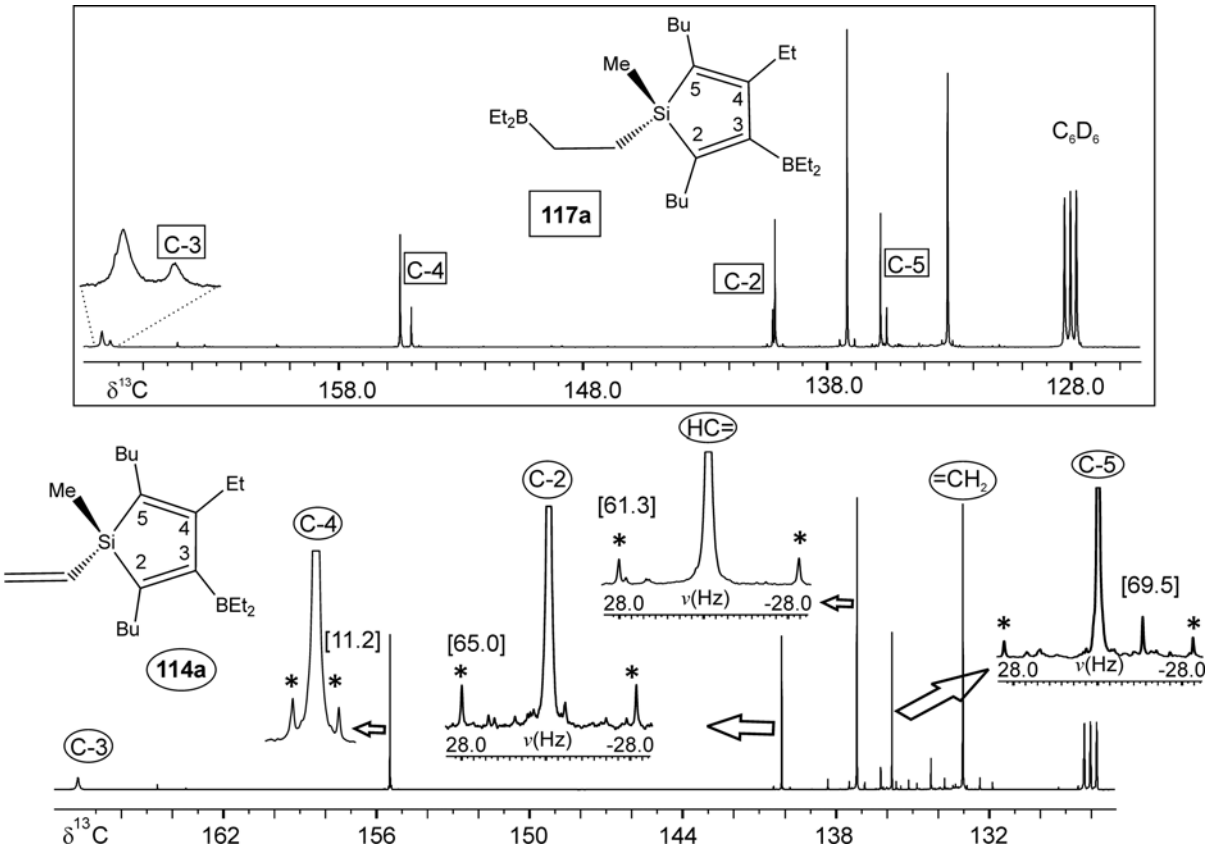
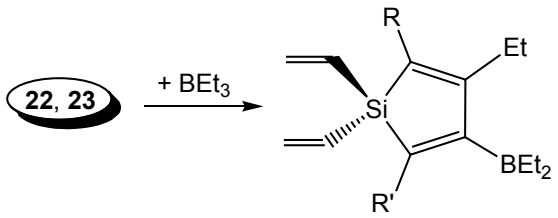


Figure 6.3. Part of $^{13}C\{^{1}H\}$ NMR spectra (100.5 MHz) of **114a** (lower trace) after 3 d of heating at 100 - 120 °C and mixture of **114a** and **117a** (upper trace) after 13 d at the same temperature. The signals belonging to Si-vinyl group disappear after 13 d. Expansions are given for ^{13}C NMR signals showing ^{29}Si satellites corresponding to $^{1}J(^{13}C,^{29}Si)$ and $^{2}J(^{13}C,^{29}Si)$.

6.4. 1,1-Ethylboration of dialkyn-1-yl(divinyl)silanes

In previous reactions one Si-vinyl and Si-allyl groups were studied and it was observed that these groups are more stable and do not take part in reactions in the presence of Si-C≡C- functional groups. After all the Si-C≡C- bonds are utilized in the

process of 1,1-ethylboration, the Si-vinyl group gets ready for relatively slow reaction. The reactivity of dialkyn-1-yl(divinyl)silanes such as **22** and **23** with BEt_3 was the next goal, and it was expected that the Si-vinyl groups will remain unchanged. In this context, the reactions of dialkyn-1-yl(divinyl)silanes (**22**, **23**) with BEt_3 were studied under stringent reaction conditions as discussed for siloles **102 - 116**. As expected, the reactions of dialkyn-1-yl(divinyl)silanes with BEt_3 led to clean formation of 1,1-(divinyl)siloles **119** and **120** (Scheme 6.6).



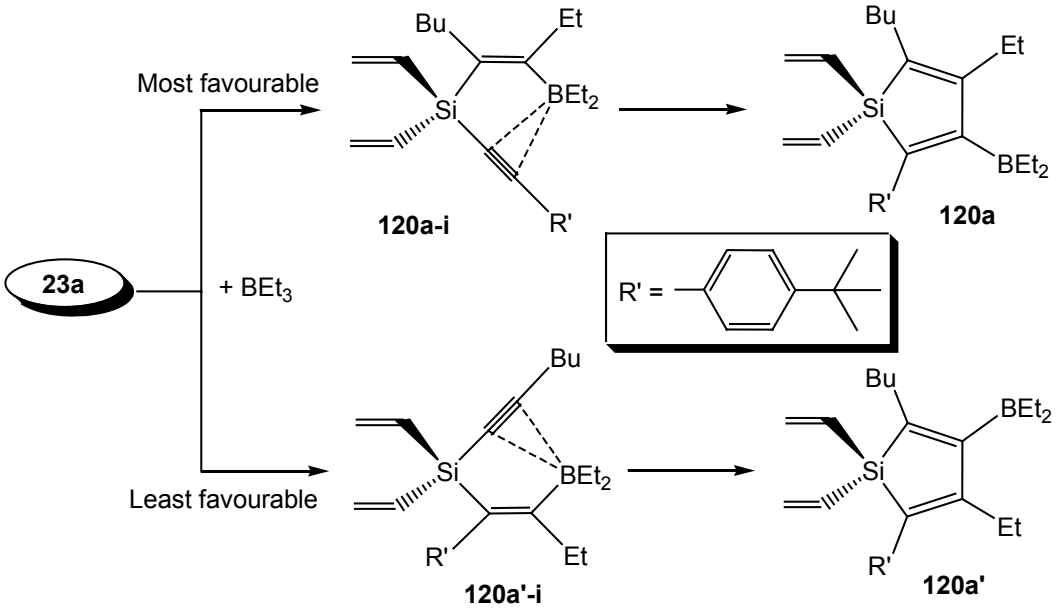
119a, **c**, **e**, **120a**
R = Bu, Ph, 4-^{t}Bu-C_6H_4, Bu
R' = Bu, Ph, 4-^{t}Bu-C_6H_4, 4-^{t}Bu-C_6H_4

Scheme 6.6. Reaction of silanes **22** and **23** with BEt_3. Formation of 1,1-divinylsiloles.

The reaction proceeds selectively *via* intermolecular 1,1-ethylboration of one of the Si-C≡C- bonds (slow step). This slow step is followed by intramolecular 1,1-vinylboration (a fast step) and the result is the formation of siloles (**119** and **120**). The reactions were stopped after a certain period of time when the silole formation was completed (monitored by ^{29}Si NMR). The siloles synthesized in this series of reactions are attractive, as they possess two exocyclic Si-C=C units in addition to endocyclic C=C double bonds. A variety of groups on C-2 and C-5 can be included, these groups may be identical as in **119a**,**c**,**e** or different as in **120a**. It can be concluded that syntheses of siloles *via* 1,1-ethylboration is fairly efficient, if its simplicity is considered. The purity as well as yield is satisfactory (ca. 95% and 90%, respectively). A single purification process in the beginning and negligible or no side reactions are the two excellent aspects of this method.

The silane **23a** bears two different organyl groups i.e., Si-C≡C-Bu and Si–C≡C-(4-^{t}Bu-C_6H_4). The bulky group 4-^{t}Bu-C_6H_4 hinders 1,1-ethylboration as compared to Bu group. In the reaction solution two isomerss were detected, unsymmetrical siloles **120a** (principle product) and **120a´** (minor component). A second set of ^{13}C and ^{29}Si NMR signals can readily be assigned to silole **120a´**. The 1,1-ethylboration mainly takes place at the Si-C≡C-Bu group but the Si-C≡C-(4-^{t}Bu-C_6H_4) group also offers

some reactivity and allows 1,1-ethylboration (Scheme 6.7). Both the intermediates **120a-i** and **120a´-i** (both not detected) rearrange into siloles **120a** and **120a´**.



Scheme 6.7. Competition between Bu and 4-^{t}Bu-C_6H_4 to allow 1,1-organoboration.

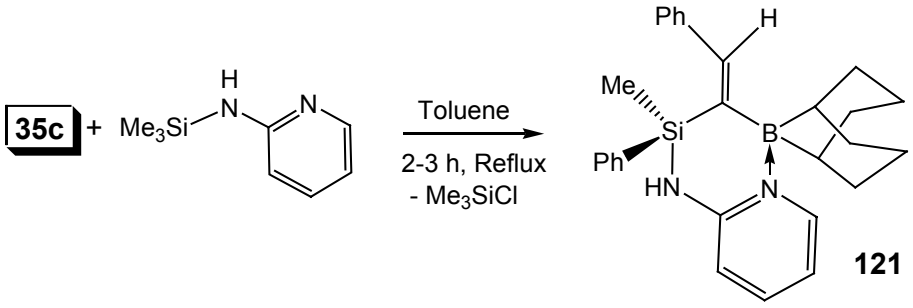
NMR spectroscopic data

Structural elucidation was based on multinuclear NMR data (^{11}B, ^{13}C, ^{1}H and ^{29}Si) measured at ambient temperature (23 °C). A complete set of NMR spectroscopic data (^{11}B, ^{13}C and ^{29}Si) for 1,1-divinylsiloles **119** and **120** is presented in Table 6.5 and ^{1}H NMR are given in Experimental section. An overview of the data shows a complete agreement with the previously listed data for siloles in this work (Table 6.1, Table 6.3 and Table 6.4). The assignments of signals regarding silole ring carbons are self-evident, strongly based on coupling constants J(^{13}C,^{29}Si) and broadened ^{13}C((BEt$_2$)C-3) NMR signals. All the coupling constant values were compared with the values obtained for the siloles discussed so far and were found in close agreement. In ^{1}H and ^{13}C NMR spectra, the vinyl groups of siloles are clearly indicated.

7. REACTIVITY OF NOVEL BORYL-SUBSTITUTED SILANES

7.1. Reaction of 9-BBN-substituted alkenylsilane with 2-(*N*-trimethylsilyl-amino)-pyridine.

The silane **35c** is attractive as it has two nucleophilic centres, one on silicon atom and the other on boron. In similar silanes the Si-Cl function has been substituted by -C≡C-R group (R = Ph, $SiMe_3$) in this work.[111] Synthetic routes and complete reaction mechanisms of the resulted compounds, 1-silacyclobutenes were fully explored. The boryl-substituted silanes similar to **35c** in structural aspects have been used for for B-N and Si-N bond formation.[50,129] A number of reactions of such alkenylsilanes with lithiated nitrogen-containing compounds have been reported.[130] It was expected that the Si-Cl function in silane **35c** can be substituted by a –N- group on treatment with molecule containing -N-$SiMe_3$ moiety. It was treated with 2-(trimethylsilylamino)pyridine in toluene at reflux temperature (120 °C) for 2 - 3 h (Scheme 7.1). The Si-Cl function was smoothly removed in the form of Me_3SiCl and a new Si-N- bond was established. It is already mentioned that the molecule of **35c** bears two electrophilic centres on silicon (Si-Cl, utilized) and on boron atom. In the molecule of 2-aminopyridyl derivative the second endocyclic nitrogen atom is capable to donate its lone pair of electrons to boron. The result is a six-membered (Si-N-C-N-B-C) ring **121**, soluble in benzene and partially soluble in pentane and hexane. The NMR data were collected in the same solvent and single crystals suitable for X-ray crystallography were recovered from the same solution.



Scheme 7.1. Reaction of silane **35c** with 2-(trimethylsilylamino)pyridine.

NMR spectroscopic results

The NMR data (^{11}B, ^{13}C, ^{29}Si) for the compound **121** are given in Table 7.1. The data show that the main features of the molecule, evident from the solid state

structure are maintained in solution. The ^{11}B NMR signal at δ –0.4 ppm is in the typical range for four-coordinated boron atoms. From ^{13}C NMR spectra it is clear that the rotation of 9-BBN is strictly restricted and a new bond (B-N) has been established, as all ^{13}C nuclei exhibit different chemical shifts. All other ^{13}C NMR signals were found within the expected range.

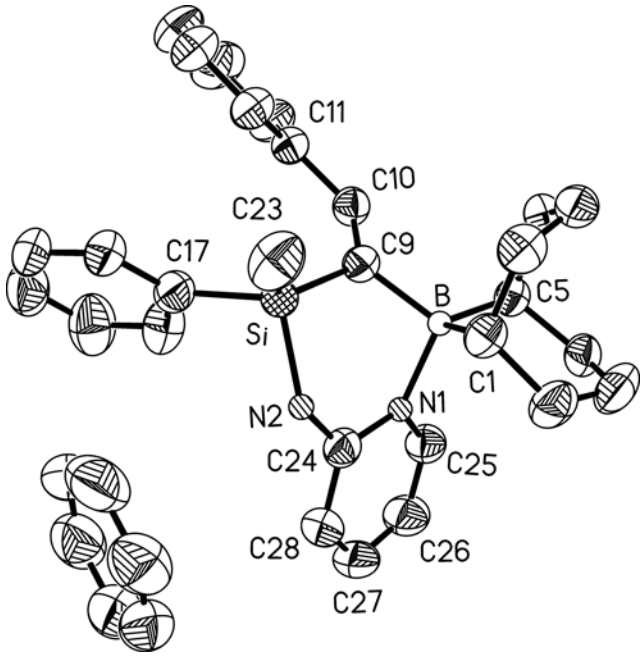


Figure 7.1. Molecular structure of **121** (ORTEP plot, 40 % probability level, hydrogen atoms are omitted for clarity). Selected bond lengths (pm) and angles (deg): Si-N2 177.9 (2), Si-C9 185.1 (2), Si-C23 186.0 (3), Si-C17 188.3 (3), N1-C24 135.3 (3), N1-B 166.3 (3), N2-C24 136.3 (3), B-C5 163.4 (3), B-C1 163.4 (3), B-C9 163.9 (3), C9-C10 134.6 (3), N2-Si-C9 100.6 (9), N2-Si-C23 105.8 (12), C9-Si-C23 120.0 (13), N2-Si-C17 104.4 (11), C9-Si-C17 114.2 (10), C23-Si-C17 109.9 (14), C24-N1-B 121.0 (18), C24-N2-Si 126.7 (15), C5-B-C1 103.4 (18), C5-B-C9 116.9 (17), C1-B-C9 113.4 (18), C5-B-N1 112.1 (17), C1-B-N1 108.5 (16), C9-B-N1 102.6 (16), B-C9-Si 111.8 (13), N1-C24-N2 118.8 (2).

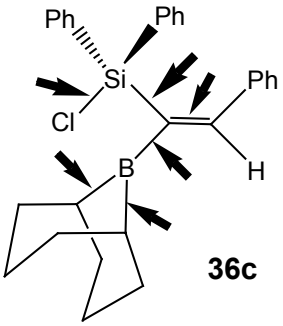
*X-ray structure analysis of **121***

The molecular structure of **121** is shown in Figure 7.1, together with selected parameters. The data relevant to crystal structure determination is listed in

Table 7.2. The molecule of **121**, has the principle plane composed of six atoms (B, 2C, 2N and Si). Four atoms (C24, N1, C9 and Si) of the six-membered ring are almost in the same plane with slight deviation of 3.03 pm. The atoms N2 and B are out of the plane (27.95 pm and 81.84 pm, respectively) in the same direction. The CBC plane of 9-BBN is almost perpendicular to six-membered ring making an angle of 88.1° and the geometry around boron atom is tetrahedral. In the compound **121** ∠ Si-C9-B is contracted by 7.59° as compared to its precursor **35c**. The endocyclic angle (∠ C9-Si-N2 = 100.59°) is expectedly smaller than the exocyclic one (∠ C17-Si-C23 = 109.85°). The B-N bond (166.3 pm) is longer than the analogous six-membered ring (163.2 pm).[131] In the latter example, the BEt_2 group is comparatively less bulky as compared to 9-BBN in **121**. In contrast the Si-N bond is longer (179.1 pm) in the reported analogue than the same bond (177.9 pm) in **121**.

7.2. Oxidation and hydrolysis

Several reactive sites are present in the molecule of **36c** ((Z)-9-[1-(chlorodiphenylsilyl)-2-phenyl-vinyl]-9-borabicyclo[3.3.1]nonane) indicated by arrows (Scheme 7.2). Among these B-C= and Si-Cl functions are sensitive towards hydrolysis, all the three B-C bonds are sensitive towards oxidation and C=C bond may also get involved in the reaction with protic reagents. Compound **36c** was subjected to slow oxidation and hydrolysis in hexane and two crystalline materials **122** and **123** were isolated. The dialkylborinic acid, 9-hydroxy-9-borabicyclo[3.3.1]nonane **122** was an expected product as a result of hydrolytic cleavage of the B-C= bond. Compound **122** has been proposed as reaction product of 9-BBN derivatives, in several reports,[132 - 134] and its synthesis has been described in a review.[135] In pure form it has also been used in some reactions.[136,137] A survey of the literature has not revealed any crystallographic studies of **122**. The compound **122** crystallizes as colorless needles along the walls of the Schlenk. The crystals were obtained at room temperature but melting point was not determined. The crystals sublime prior to be sealed in capillary.



36c

Scheme 7.2. Formula of **36c**, the arrows show the bonds which can take part in the reaction and are sensitive to oxidation and hydrolysis.

The second crystalline material isolated was a macrocyclic molecule **123** composed of a twelve-membered bicyclic skeleton, an unexpected product. The formation of this molecule is not straightforward, it is the result of hydrolysis, oxidation, self-assembly and condensation of boric acid and polysiloxane. It is well known that polysiloxane with boroxanes are useful materials as protective coatings,[138 - 140] for which any well defined species have never been isolated. The attempt to get defined crystalline materials by reacting Ph_2SiCl_2 with $B(OH)_3$ in the ratio of 3:1 under reflux using toluene as the solvent, gave no such results. Therefore, the term “self-assembly” was used.

NMR spectroscopic studies

Compound **122** has already been characterised by NMR spectroscopy.[141] Since compound **123** is sparingly soluble in $CDCl_3$, its ^{1}H, ^{11}B, ^{13}C and ^{29}Si NMR data were determined (Table 7.1 and Experimental). These data indicate that the main features of the solid-state structure are retained in solution. In particular, the ^{11}B and ^{29}Si chemical shifts ($\delta^{11}B$ = 17.3 and $\delta^{29}Si$ = -41.4) are characteristic for the respective surroundings of boron and silicon atoms.

*X-ray crystallographic studies of **122** and **123***

Molecular structures of **122** and **123** are shown together with selected bond lengths and angles in Figure 7.2 and Figure 7.3, respectively. The data pertinent to crystal structure determination are listed in Table 7.2. In the lattice, the molecules of **122** are associated by O-H-O hydrogen bridging (O1-O2 = 270.5 pm and O2-O3 = 267.6 pm), forming a chain. This is in contrast to the heavy congeners with sulfur and selenium, for which dimers have been characterized in the solid state.[142] In compound **122**, the trigonal planes C9C13O1B1 and C1C5O2B2 around the boron atoms are almost perpendicular (87.3°) to each other, while the C17-C21-B3-O3

plane is twisted by an angle of 22.1° against the C9-C13-O1-B1 plane. The C-C bonds starting from the bridge head carbon atoms C9 and C13 are elongated when compared with those starting from C11 and C15. This effect is less pronounced for 9-organo-9-BBN derivatives.[45,111,112,143,144] These alternating C-C bond lengths can in principle be traced to hyperconjugation involving the boron p_z orbital and the C-Cσ bonds.[120,121]

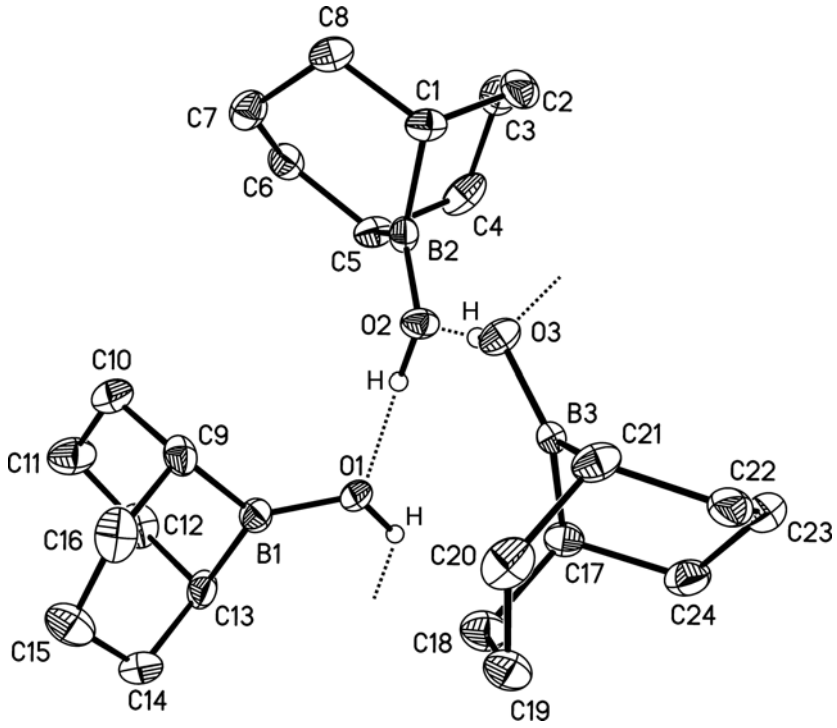


Figure 7.2. View of the three molecules of 9-hydroxy-9-borabicyclo[3.3.1]nonane **122** in the crystal, associated *via* intermolecular H-O-H bridges (ORTEP plot, 50 % probability level, hydrogen atoms except OH are omitted for clarity) bond lengths (pm) and angles (deg): B1-C9 154.3 (6), B1-C13 155.0 (6), B1-O1 136.3 (5), C9-C10 153.9 (6), C10-C11 149.8 (7), C11-C12 148.3 (6), C12-C13 155.7 (6), C13-C14 154.1 (7), C14-C15 151.2 (7), C15-C16 152.0 (7), C16-C9 154.8 (7), C16-C9-C10 112.4 (4), C14-C13-C12 113.0 (4), C10-C11-C12 116.6 (5), C14-C15-C16 116.2 (5), C16-C9-B1 108.6 (4), C10-C9-B1 107.4 (4), C12-C13-B1 105.5 (4), C14-C13-B1 109.5 (4), O1-B1-C9 121.0 (4), O1-B1-C13 126.7 (4), C9-B1-C13 112.3 (4).

The Si-O and B-O bond lengths in **123** are in the expected range,[145] with the Si-O bonds in the Si-O-Si units being slightly shorter than in Si-O-B units. The surroundings of the silicon atoms are close to tetrahedral, whereas the surroundings of each boron atom are trigonal planar. The bond angles Si-O-Si are significantly

wider than the B-O-Si angles. Bond angles Si-O-Si are extremely sensitive to subtle effects, in inorganic solids or in molecular organosilicon compounds.[146 - 149] Sometimes they may change for the same molecule with the solvent used for crystallization.[150]

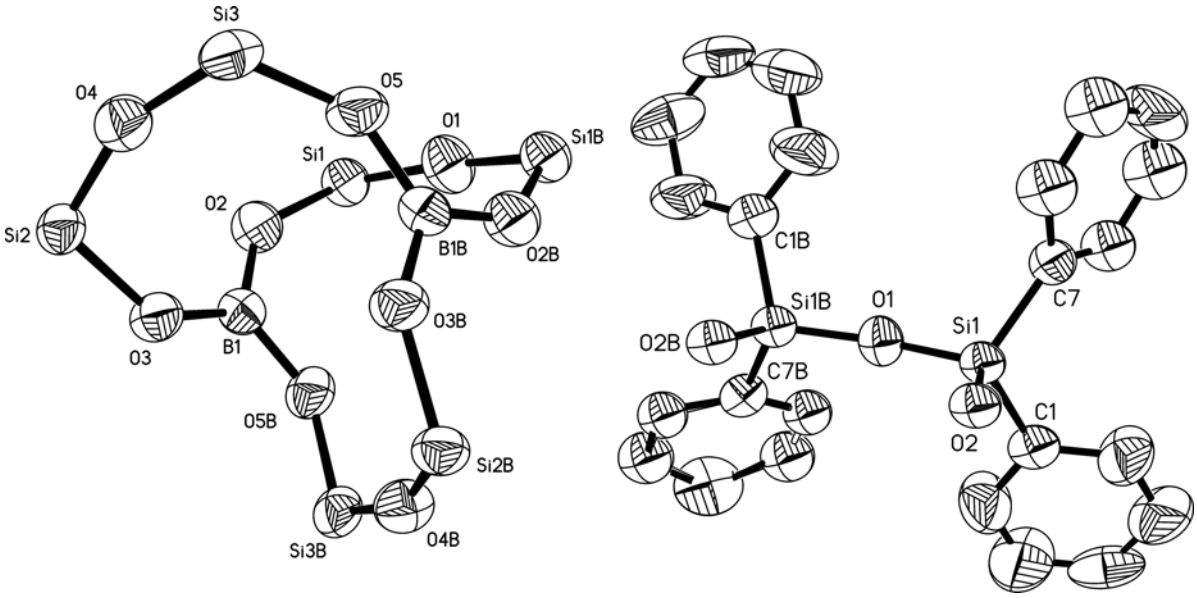
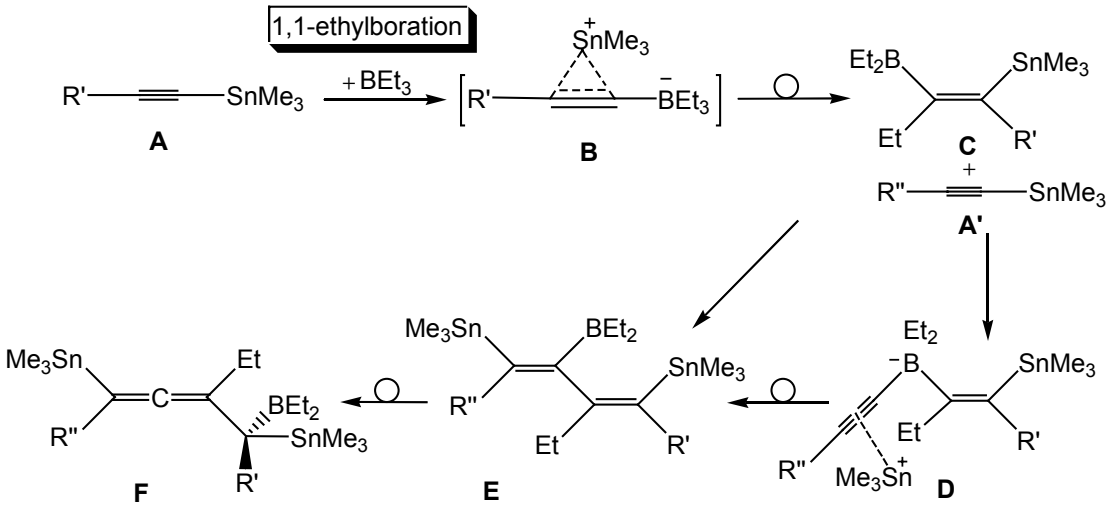


Figure 7.3. Skeletal atoms of macrocycle, diborabicyclo[5.5.5]heptadecane-type molecule **123** (left view, ORTEP plot, Ph groups are omitted for clarity). The figure (right view) shows the arrangement of Ph groups around the Si atom. Selected bond lengths (pm) and angles (deg): B1-O2 135.2 (5), B1-O5 135.7 (5), B1-O3 135.6 (5), Si1-O1 161.0 (13), Si1-O2 163.1 (3), C1-Si1 185.7 (5), C7-Si1 185.6 (5), O2-B1-O5 118.9 (3), O2-B1-O3 120.6 (4), O5-B1-O3 120.4 (4), O1-Si1-O2 108.9 (19), O1-Si1-C1 110.5 (18), O2-Si1-C1 105.0 (17), C1-Si1-C7 111.1 (2), B1-O2-Si1 137.2 (3), Si1-O1-Si1B 166.3 (3).

7.3. Reactions of alkenylsilanes with bis(trimethylstannyl)ethyne

Alkenylsilanes similar to **37 - 40** have been used for further transformations and were shown to lead to some novel heterocyclic compounds (Scheme 1.5). Silyl- and stannyl-substituted allenes and butadienes[75,151] have been prepared by the reaction of respective silyl- or stannyl-substituted alkenes and bis(trimethylstannyl)alkyne or trimethyl(propyn-1-yl)stannane. The respective Sn analogues have been prepared by the reaction of alkyn-1-ylstannannes with BEt_3.[152] The reactions proceed in two steps. In the first step, 1,1-ethylboration of the alkyn-1-ylstannane leads to alkenylstannane **C**, followed by the reaction of one equivalent of alkyn-1-ylstannane

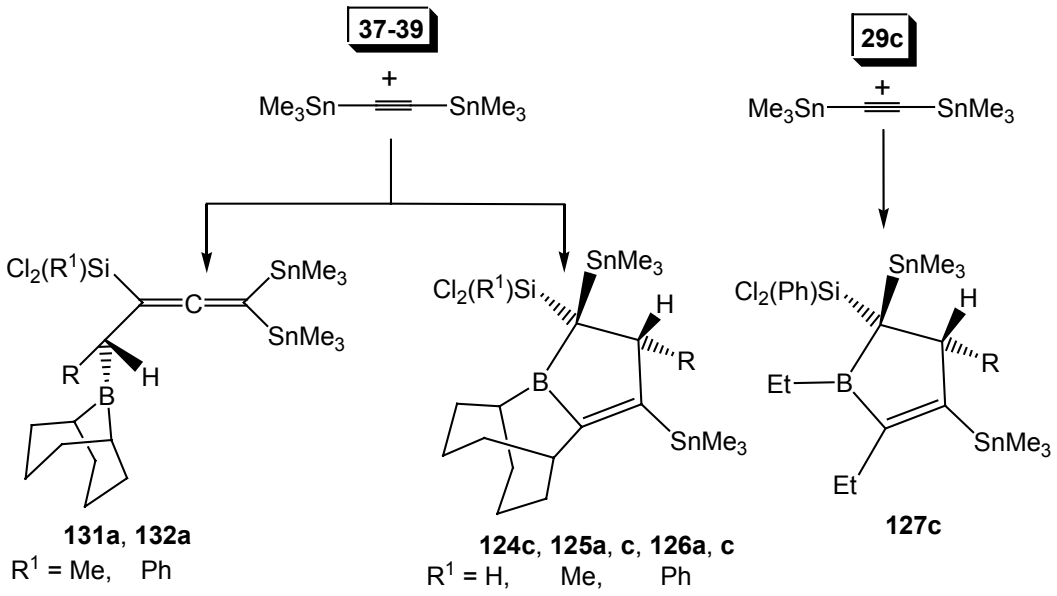
A´ at high temperature (75 - 120 °C), affording allenes **F**. Some intermediates (**B**, **D** and **E**) are proposed in Scheme 7.3. They rearrange into the final products and have not been detected in reaction solutions. The products of such reactions allenes and butadienes have been studied and characterized in solution together with solid state structure of allene compound.[153]



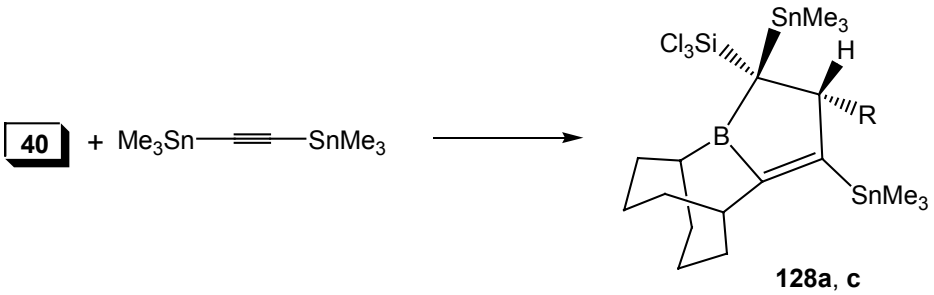
Scheme 7.3. Complete reaction mechanism for the synthesis of some allenes, reported by B. Wrackmeyer.[152]

Considering the unique reactivity of Si-Cl functions (Scheme 3.1 and Scheme 3.5), the bis(trimethylstannyl)ethyne was treated with alkenyl(dichloro)silanes **37 - 39** at ambient temperature using hexane, pentane or benzene as solvents. Based on literature survey one expects mainly the formation of allenes or butadienes or a mixture containing both.[152,153] Treatment of alkenes bearing the $Cl_2(R^1)Si$- moiety (R^1 = H, Me, Ph) **37** - **39** with bis(trimethylstannyl)ethyne was surprising, since these reactions took a new direction. Pure borolenes **124 - 126** or mixture of borolenes and allenes (in some reactions) were the principle products. It is noteworthy that the Si-Cl functions play the key role in such reactions, on the other hand the effect of ≡C-Ph group in the starting alkyn-1-ylsilane appears also to be of prime importance. Two organyl groups on Si-C≡C-R carbon atom were used (R = Bu and Ph). The NMR spectroscopic data revealed that the Bu group affords a mixture, mainly containing the allenes **131** and **132** (70 - 95 %) accompanied by borolenes (5 - 30 %) as side products. Both the fractions in the mixture could readily be identified as they possess distinct NMR chemical shifts (^{13}C, ^{29}Si and ^{119}Sn). The alkenylsilanes bearing Ph group afford clean formation of borolenes **124 - 126**. The role of organyl group was

very clear in these reactions (Scheme 7.4). The question was, whether these groups (R = Bu, Ph) will maintain the same behaviour if the starting alkyn-1-ylsilanes bear the $SiCl_3$ moiety. Therefore, alkenylsilanes **40** were considered in next reactions, and the reactions were carried out applying the same reaction conditions. This resulted in clean formation of borolenes **128** and no allenes were detected in the reaction mixtures (Scheme 7.5).



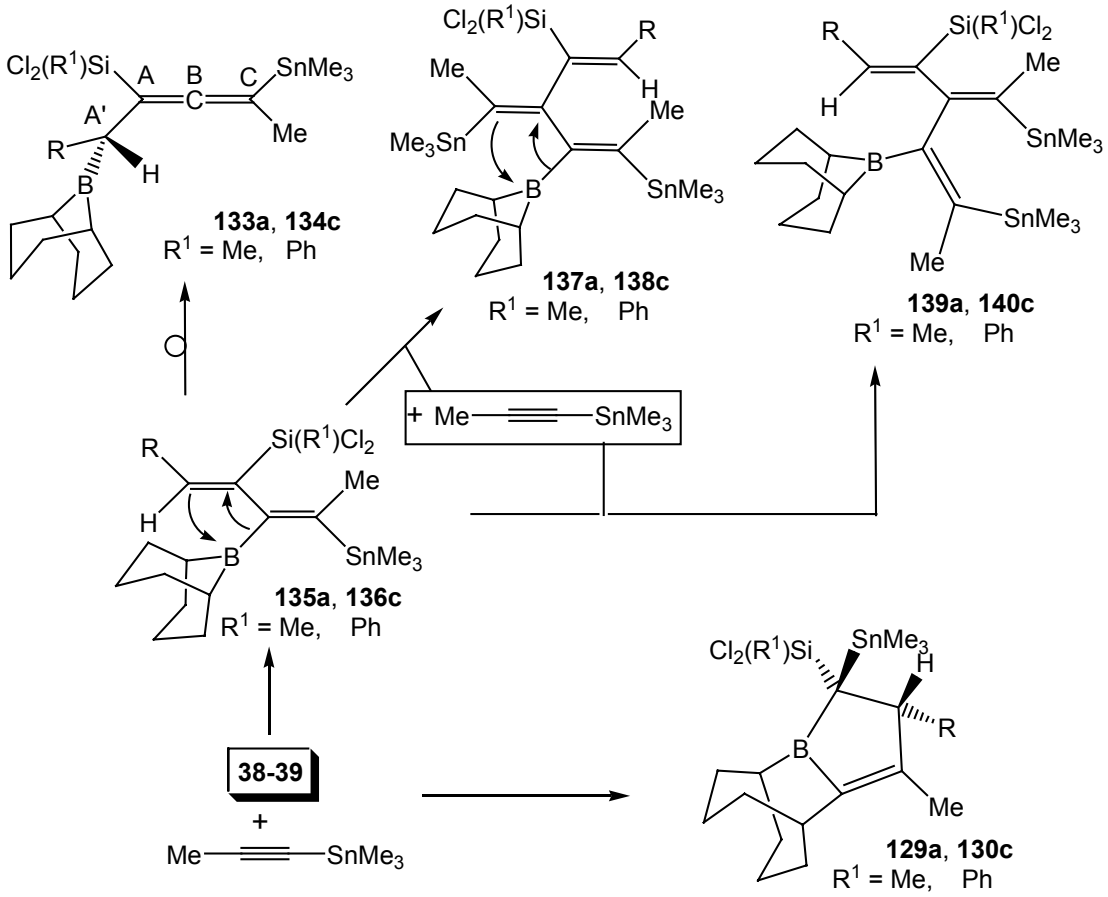
Scheme 7.4. Two practical routes of reaction between $C_2(SnMe_3)_2$ and silanes **29** and **37 - 39**.



Scheme 7.5. Reaction of alkenyl(trichloro)silanes **40** with bis(trimethylstannyl)ethyne leading selectively to borolenes **128**.

The reactions of boryl-substituted alkenylsilanes (**37 - 40**) to afford borolenes are new findings and such compounds have not been reported so far at least by following the process of 1,2-hydroboration. Having established a better method of synthesis for borolenes, the studies were extended to reactions of trimethyl(propyn-1-

yl)stannanes with silanes **38** and **39** as discussed above. Two test reactions were carried out observing the same reaction conditions. The reactions lead to a number of compounds as a mixture of borolenes **129**, **130** (principle products) allenes **133**, **134** and butadiene derivatives **135 – 140**. In the mixtures major components (borolenes **129**, **130**) could easily be identified from their characteristic NMR data (^{13}C, ^{29}Si and ^{119}Sn). The reaction mixture contains some unidentified products. It was not possible to assign all the signals precisely to the corresponding nuclei. Principle fractions of the mixture were identified from their finger print regions in ^{13}C (olefinic region), ^{29}Si and ^{119}Sn NMR spectra.



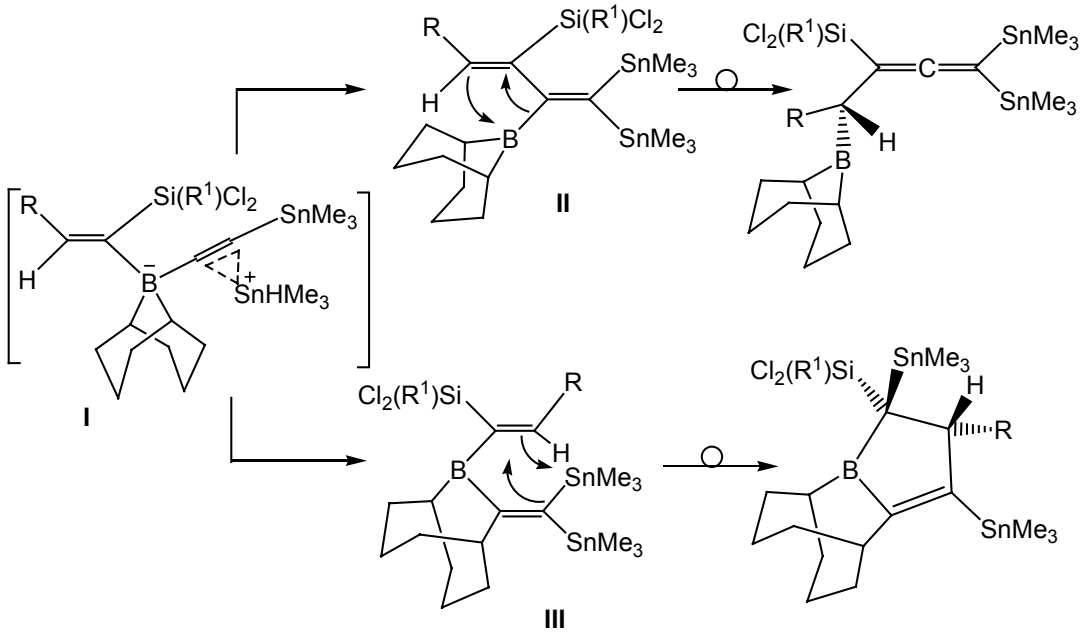
Scheme 7.6. Products from the reaction of trimethy(propyn-1-yl)stannane with alkenylsilanes, **37** and **38**.

It can be concluded that Si-Cl functions are the major contributors in such reactions to afford selectively borolenes **124 – 128**, and at the same time the role of the group R in such selectivity appears to be important. The new compounds were oily liquids except **124c** and **126c** which were crystalline solids. All the compounds

were studied by multinuclear NMR spectroscopy (^{11}B, ^{13}C, ^{1}H, ^{29}Si and ^{119}Sn) and two members of the series **124c** and **127c** were studied in solid state by X-ray crystallography.

Reaction mechanism

The proposed reaction mechanism for the two possible routes of reaction is shown in Scheme 7.7. First the zwitterionic-like intermediate **I** is formed. This intermediate follows two routes upon rearrangements and leads to two other intermediates (**II** and **III**). In intermediate **I**, the migration of -C≡C-R bond from boron to olefinic carbon (C=C) atom gives an expected candidate **II** (Scheme 7.3). There is also another possibility that one of the B-C bond (9-BBN) is activated and the -C≡C-R bond migrates to the B-C carbon atom (9-BBN) resulting into a divinylborane-like intermediate **III**. This intermediate causes ring enlargement of the 9-BBN system. In the next step, both intermediates lead to different products, *e. g.* **II** affords allene derivatives and **III** leads to borolenes. Both intermediates (**II** and **III**) are unstable and could not be detected in reaction solution.



Scheme 7.7. Two possible reaction path ways leading to allenes or borolenes.

NMR spectroscopic studies

The NMR data (^{11}B, ^{13}C, ^{29}Si and ^{119}Sn) regarded borolenes, **124 – 130**, allenes **131 – 134** and butadienes **135**, **136** are listed in Table 7.3 to Table 7.5. The

^{1}H and other relevant data are collected in Experimental section. The NMR data set is consistent with the proposed structures. The interpretation was strongly based on various NMR parameters in solution state, *i. e.* coupling constants, {J(^{13}C,^{119}Sn)}, [J(^{13}C,^{29}Si)], [[J($^{119/117}$Sn,$^{119/117}$Sn)]] and [(J(^{29}Si,^{119}Sn))] (see Table 7.3 to Table 7.5). The ^{13}C spectra of borolenes show two signals at high frequency, a broad one and a sharp. They can be tentatively assigned to B-C(2)= and =C(3) carbons on the basis of characteristic range for these ^{13}C nuclei: {^{1}J(^{13}C,^{119}Sn)} ≈ 400 Hz and {^{3}J(^{13}C,^{119}Sn)} ≈ 12 Hz (Table 7.4 contains exact values). Other ^{13}C NMR signals of the borolene rings appear in higher field. The assignments of ^{13}C NMR signals belonging to these carbons are straightforward (Figure 7.4). The C-4 is linked to boron and gives a broadened ^{13}C NMR signal with satellites for ^{2}J(^{13}C,^{119}Sn). According to ^{13}C NMR data the 9-BBN bicyclic ring is enlarged in such a way that one B-C bond has been cleaved and a new (9-BBN)C-C= has been formed. This carbon of 9-BBN is marked as C(2´) (Figure 7.4) and can easily be identified by $^{117/119}$Sn satellites. Owing to ring enlargement of 9-BBN, the surroundings of all carbon atoms are changed and they exhibit different ^{13}C NMR frequencies including a broad ^{13}C-B signal. The ^{13}C signal for R and R^{1} as well as $SnMe_3$ groups are in the expected range. Similarly the ^{13}C NMR data of allenes are very informative and the three carbons of main allene stem C=C=C (**A - C**) are self-evident because they possess $^{119/117}$Sn satellites. The carbon '**B**' is particularly easy to be assigned as it possesses {^{2}J(^{13}C,$^{119/117}$Sn)} satellites belong to two different $^{119/117}$Sn atoms as well as a typical chemical shift at high frequencies. (Figure 7.6). The ^{11}B chemical shifts cover a relatively broad range ca. δ = 85 - 70 ppm. The chemical shift δ ≈ 10 ppm to higher field is typical range for such five-membered boron compounds.[154] The ^{29}Si and ^{119}Sn NMR spectra are equally important in monitoring the progress of the reactions and structural assignments. In the ^{119}Sn NMR spectra of borolenes satellites due to J($^{119/117}$Sn,$^{119/117}$Sn) are visible even across four bonds (35 - 40 Hz). Respective ^{29}Si satellites for J(^{29}Si,$^{119/117}$Sn) appeared with approximately the same value of ca. 40 Hz; they could also be measured from $^{117/119}$Sn satellites in the ^{29}Si NMR spectra (Figure 7.5 and Figure 7.7). The ^{119}Sn NMR data of allenes are useful for measuring ^{2}J(^{119}Sn,^{117}Sn) and ^{2}J(^{119}Sn,^{119}Sn) (Figure 7.7).

Reactions of silanes **38a** and **39c** with trimethyl(propyn-1-yl)stannane afford mixtures of compounds containing borolenes as the principle product accompanied by allenes (**133a**, **134c**) and butadienes (**135a**, **136c**). Structures of these

compounds were proposed on the basis of their characteristic NMR data. The aliphatic region (-10 to 40 ppm) in ^{13}C NMR spectra does not give useful information, owing to the large number of signals. Most of the information were extracted from particular parts of the spectra in the range between δ 45 to 200 ppm. Signals in ^{119}Sn NMR spectra were observed at δ –44.0 and –48.0 ppm and a ^{29}Si chemical shift at δ 2.3 ppm was tentatively assigned to **138c**. Similarly in the same spectra ^{119}Sn NMR signals at δ –41.7 and –55.0 ppm (with equal intensity) and a ^{29}Si resonance at δ 0.9 ppm were assigned to compound **140c**. For these compounds **138c** and **140c** ^{13}C and ^{1}H data assignments were not possible owing to low concentration. Several small signals appeared in ^{13}C, ^{29}Si and ^{119}Sn NMR spectra, as a result of unknown side reactions. The ^{29}Si and ^{119}Sn NMR data are particularly important as the products possess distinct chemical shifts in their respective ^{29}Si and ^{119}Sn spectra. The relative intensity and satellites provide a wealth of information for appropriate assignments.

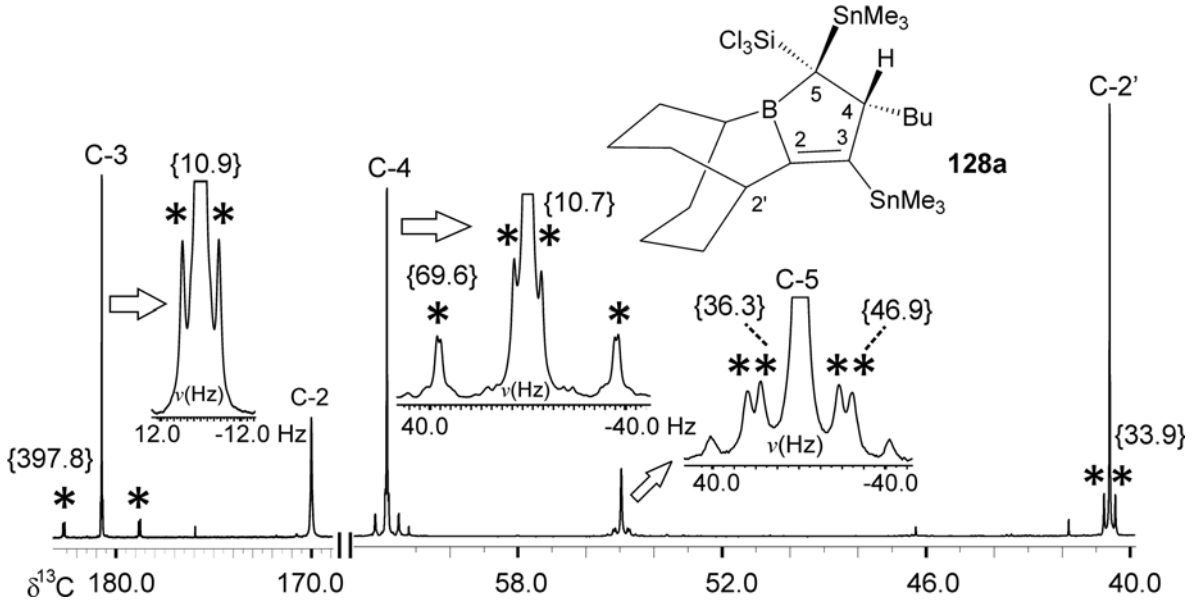


Figure 7.4. 100.54 MHz $^{13}C\{^{1}H\}$ NMR spectrum of the **128a** in C_6D_6 (15% solution v/v) at 23 °C. Expansions are shown for the signals showing $^{117/119}Sn$ satellites, marked by asterisks, corresponding to $^{n}J(^{13}C, ^{117/119}Sn)$ where n = 1, 2 or 3.

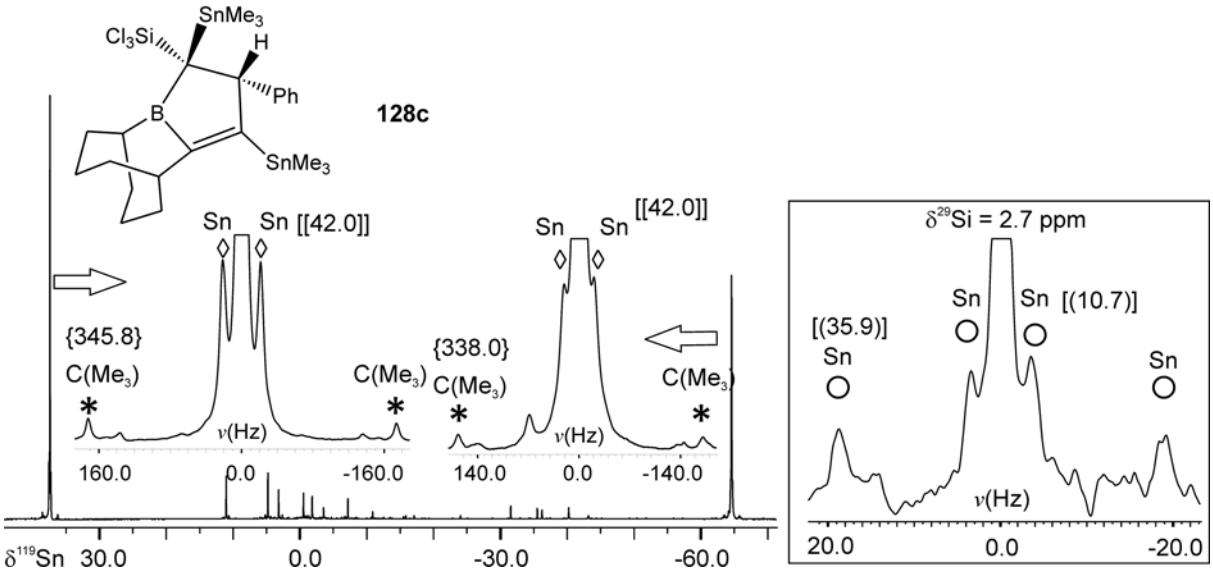


Figure 7.5. 149.1 MHz $^{119}Sn\{^{1}H\}$ (left) and 79.4 MHz $^{29}Si\{^{1}H\}$ (right inserted) NMR spectra of the **128c** in C_6D_6 (15% solution v/v) at 23 °C. Expansions are shown for the signals where respective satellites for $^{1}J(^{13}C,^{119}Sn)$, $^{4}J(^{117/119}Sn,^{117/119}Sn)$ and $^{2/4}J(^{29}Si,^{117/119}Sn)$ are marked by asterisks, diamonds and circles, respectively. In ^{119}Sn NMR spectra small fractions are visible as a result of side reactions including allenes.

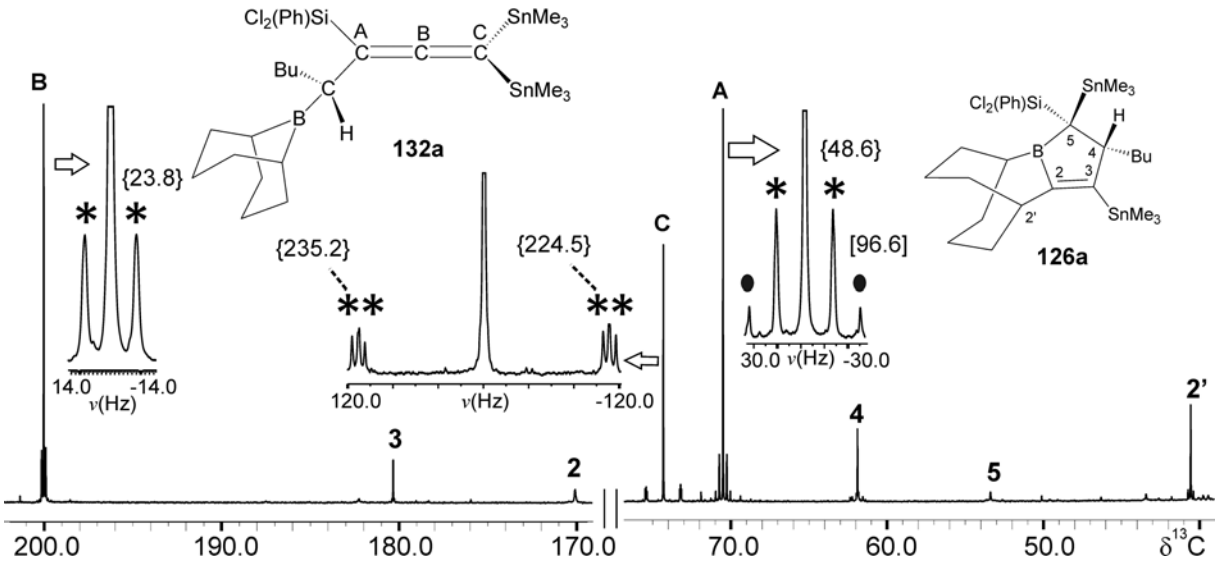


Figure 7.6. 100.54 MHz $^{13}C\{^{1}H\}$ NMR spectrum of the mixture of **126a** and **132a** in C_6D_6 (15% solution v/v) at 23 °C. Expansions are shown for the signals belonging to **132a**, showing $^{117/119}Sn$ satellites, marked by asterisks, corresponding to $^{n}J(^{117/119}Sn,^{13}C)$ where n = 1, 2 or 3. The ^{29}Si satellites, marked by filled circles, represent $^{1}J(^{13}C,^{29}Si)$.

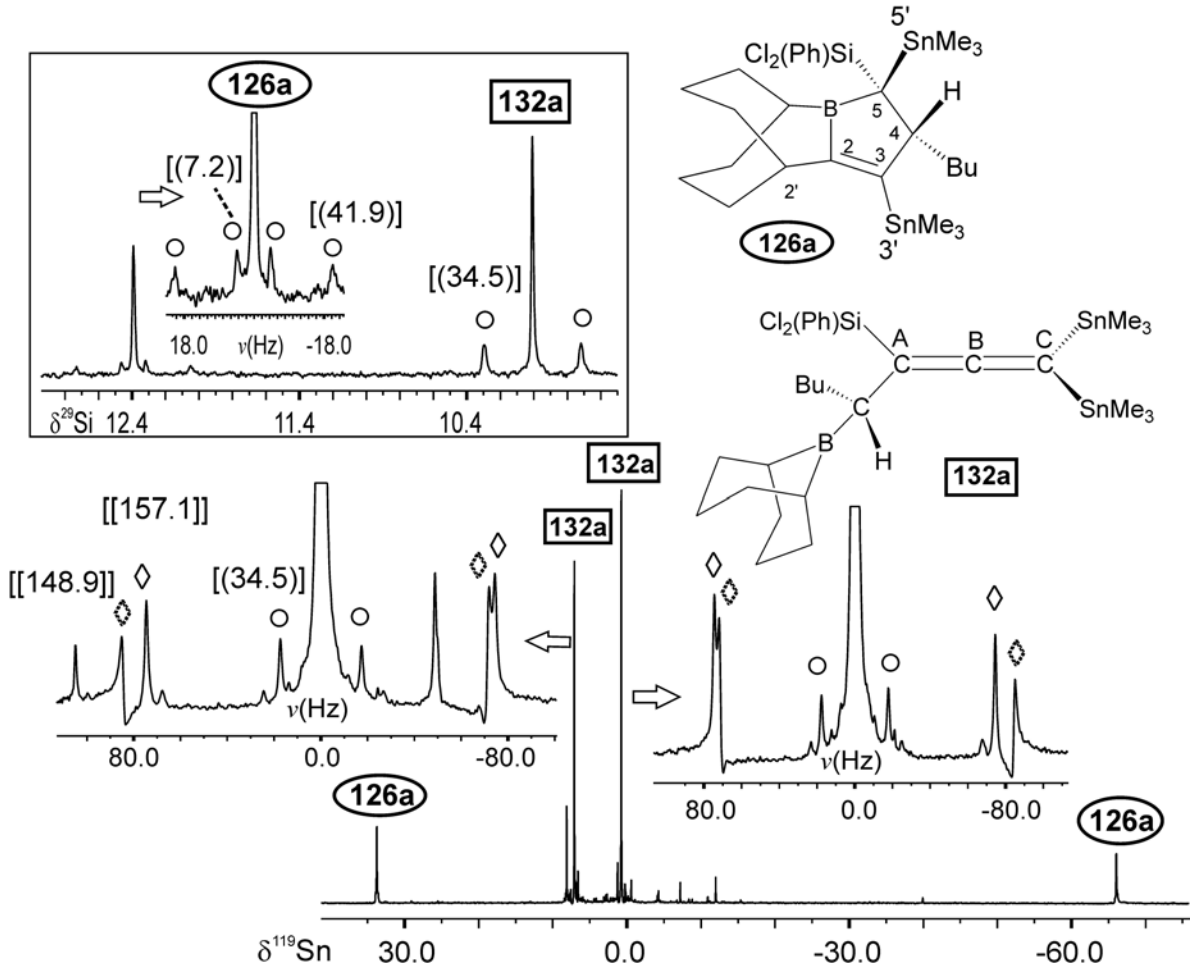


Figure 7.7. 149.1 MHz ^{119}Sn{^{1}H} (lower trace) and 79.4 MHz ^{29}Si{^{1}H} (upper insert) NMR spectra of the mixture containing borolene **126a** and allene **132a.** Expansions are given for the signals showing the respective satellites for $J(^{117/119}\text{Sn},^{117/119}\text{Sn})$ and $J(^{29}\text{Si},^{117/119}\text{Sn})$.

*X-ray structure analyses of **124c** and **126c***

Molecular structures of **124c** and **126c** are given in Figure 7.8 and Figure 7.9, respectively, selected bond lengths and angles are listed in Table 7.6 and data pertinent to X-ray structure determination can be found in Table 7.7. In the structure of **124c** the B4C atoms of the five-membered ring are almost in the same plane with a slight mean deviation of 2.6 pm. The phenyl group C20 - C25 is twisted by 75.9° against the B4C plane. Sn2 and H19 are at *cis* position while Sn1 is trans to H19. The CBCC atoms are exactly in the same plane within experimental error with trigonal planar geometry. The interatomic distance between C18-Sn2 (223.3 pm) is longer than the interatomic distance of C7-Sn1 (214.3 pm). The difference can be explained on the basis of hyperconjugation where empty p_z orbital of boron and C-

Cσ are involved.[120,121] The ∠ C13-B1-C18 is expectedly wider (132.5°) than the ∠ C17-B1-C18 (106.2°) and ∠ C17-B1-C13 (121.3°).

The crystal data of **126c** are very close to those of **124c**. All the bond lengths and bond angles are well comparable. The principle five-membered ring and CBCC atoms are situated almost in the same plane (mean deviation = 6.36 pm and 0.9. pm respectively). The phenyl group (C19 - C24) is oriented in such a way that it makes an angle of 96.2° with the principle five-membered borolene plane. All bond lengths and bond angles of 9-BBN are different, which is also evident from ^{13}C NMR data. The ∠ C15-B1-C2 of 9-BBN is wider than the other CBC angles as expected. The sum of CBC angles is 360° in both molecules **124c** and **126c** and clearly indicate that both the boron atoms are three-coordinated and are not involved in any intermolecular or intramolecular interactions.

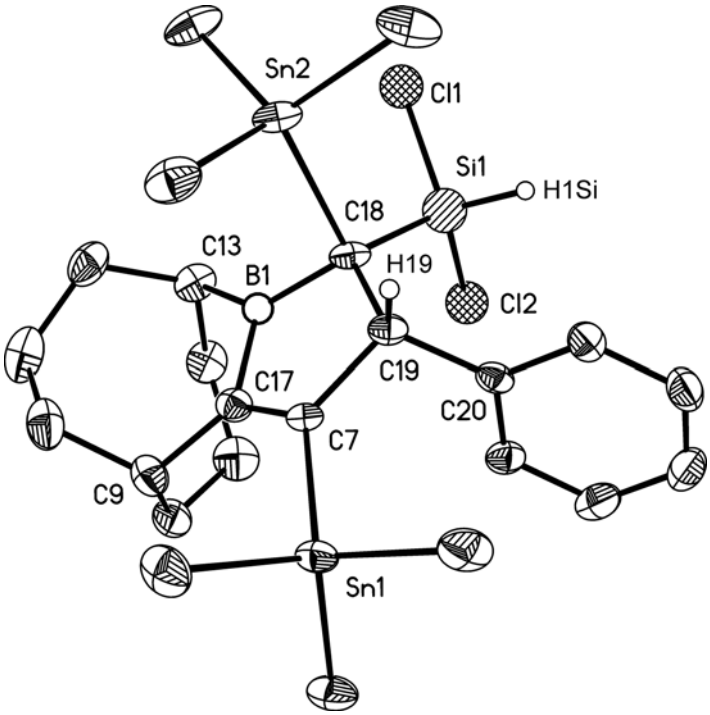


Figure 7.8. Molecular structure of **124c**; ORTEP plot (40 % probability level; hydrogen atoms except H19 and H1Si, are omitted for clarity).

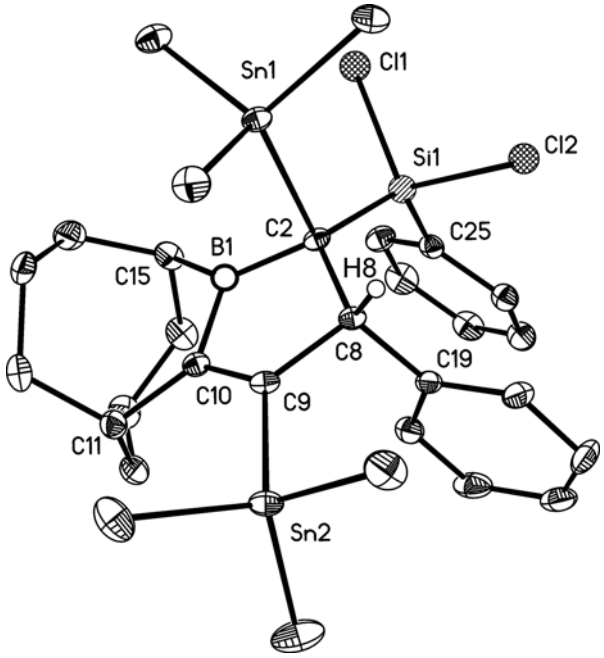


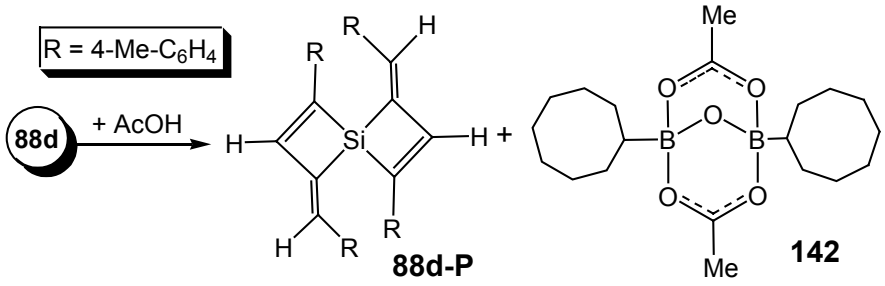
Figure 7.9. Molecular structure of **126c**; ORTEP plot (30 % probability level; hydrogen atoms except H8, are omitted for clarity).

7.4. Protodeborylation reactions of novel heterocycles.

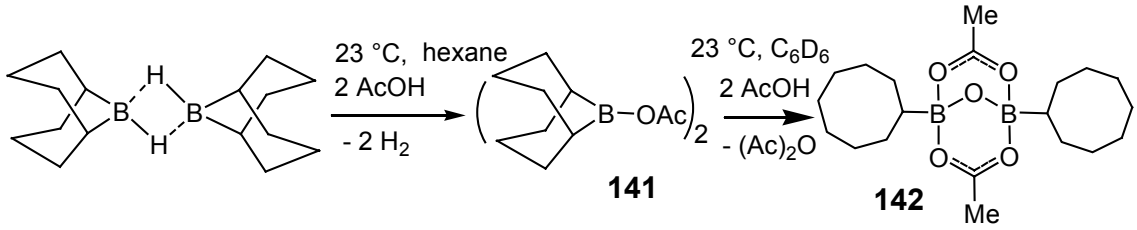
7.4.1. Reaction of boryl-substituted 4-silaspiro[3.3]hepta-1,5-diene with acetic acid

The spirosilane **88b - d** (4-silaspiro[3.3]hepta-1,5-diene derivatives) possess two 9-borabicyclo[3.3.1]nonyl groups linked to C-2 and C-6 of bicyclic rings. The boron atoms in the molecules are three-coordinated, making them air and moisture sensitive. One example **88d** was considered for protodeborylation and was treated with acetic acid at ambient temperature. The boryl group was smoothly removed. The reactions studied here (Scheme 7.8) require an excess of acetic acid in order to achieve complete protodeborylation, and it can be assumed that $(Ac)_2O$ is generated in the course of the formation of boron-oxygen compound **142**. Indeed, it has been reported that the attempted synthesis of tri(acetoxy)borane $B(OAc)_3$, frequently leads, also by elimination of $(Ac)_2O$, to $O[B(OAc)_2]_2$ which possesses a molecular structural framework analogous to **142**.[155] The formation of the boron-oxygen compound **142** was surprising, since the 9-borabicyclo[3.3.1]nonane moiety often survives various transformations involving the boron atom, although during the course of this dissertation it was observed that slow cleavage *via* oxidation/hydrolysis of all B-C bonds of an 9-alkenyl-9-borabicyclo[3.3.1]nonane[156] occurs. However, in previous

reports on the treatment of 9-borabicyclo[3.3.1]nonane derivatives with carboxylic acids, the protolysis of one of the endocyclic B-C bonds was not mentioned.[4,157 - 159] Therefore, it was of interest to study the reaction of the 9-borabicyclo[3.3.1]nonane dimer with acetic acid. The results are schematically summarized in Scheme 7.9. The stoichiometric 1:1 reaction affords the 9-acetoxy-9-borabicyclo[3.3.1]nonane dimer **141** in high yield. In the presence of an excess of acetic acid, the protolysis of one of the endocyclic B-C bonds starts immediately and is complete after 30 - 40 minutes at room temperature.



Scheme 7.8. Acetolysis of triorganoboranes containing the 9-borabicyclo[3.3.1]nonyl group (**88d**).



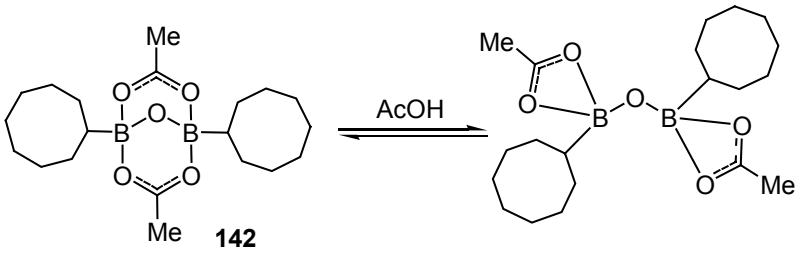
Scheme 7.9. Reaction of 9-borabicyclo[3.3.1]nonane dimer with acetic acid. The 9-acetoxy-9-borabicyclo[3.3.1]nonane **141** is formed first in high yield, followed by reaction with more acetic acid to give smoothly the compound **142** in essentially quantitative yield.

*NMR studies of **88d - P**, **141** and **142***

The NMR data of protodeborylated spirosilane **88d - P** (^{13}C and ^{29}Si), **141** and **142** (^{11}B and ^{13}C) are listed in Table 7.8 and ^{1}H NMR data of corresponding compounds are listed in Experimental part. The data show close resemblance to the proposed structures. The NMR signals (^{13}C and ^{29}Si) of the deborylated spirosilane can be assigned to the respective nuclei in a similar way as for starting boryl-containing spirosilane **88d**[160] as there are slight variations in the whole data. The disappearance of boron (^{11}B NMR spectra) and appearance of a singlet for ^{1}H(C-3) in

the olefinic region (^{1}H NMR spectra) are clear indication of the proposed structure. The ^{29}Si NMR spectrum is less informative, since the change in chemical shift is not pronounced.

The presence of cyclooctyl groups in **142** is clearly evident from the typical pattern in the ^{13}C NMR spectra which is quite different from that of 9-borabicylo[3.3.1]nonane system. In the case of **142**, the ^{13}C(CH_3-CO_2) NMR signals are broadened due to exchange. It is conceivable that the equilibrium shown in Scheme 7.10 is responsible for the exchange and the exchange may be catalyzed by unavoidable traces of acetic acid.[161]



Scheme 7.10. Potential reasons for broadened Me and CO_2 ^{13}C NMR signals of the AcO group.

*X-ray structural study of the cyclooctylboron compound **142***

The molecular structure of **142** is shown in Figure 7.10 together with selected structural parameters. The data pertinent to structural solution and refinement are listed in Table 7.10. The bond lengths and angles are in agreement with the compounds of comparable structures.[5,155,162] The surroundings of the boron atoms are distorted tetrahedral. All bond lengths and angles are in the expected range and there are only slight variations depending on the groups attached to the boron atoms. Expectedly, the cyclooctyl group in **142** does not affect the structure significantly when compared with that of **143.**[5]

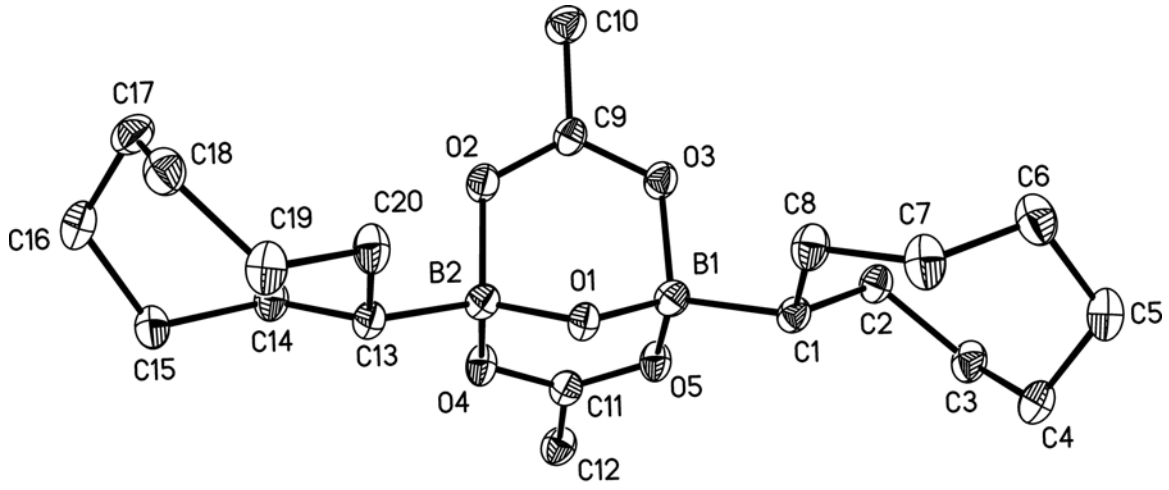
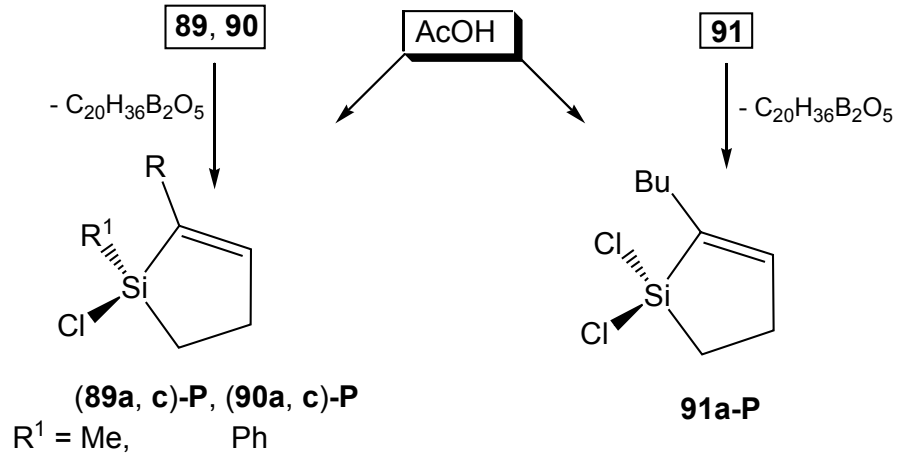


Figure 7.10. Molecular structure of the cyclooctylboron compound **142** (ORTEP, 50 % probability; hydrogen atoms are omitted for clarity). Selected bond lengths (pm) and angles (deg): B1-O1 140.0 (2), B2-O1 140.6 (2), B2-O2 158.0 (2), B1-O3 157.6 (2), C1-B1 158.6 (2), C9-O2 126.7 (2), C9-O3 126.8 (2), C9-C10 149.0 (2), B1-O1-B2 113.3 (14), O1-B2-O2 108.6 (14), C9-O2-B2 119.9 (13), O2-C9-O3 124.1 (15), C9-O3-B1 119.4 (13), O5-B1-O3 101.2 (12).

7.4.2. Protodeborylation of 1-silacyclopent-2-enes

The treatment of glacial acetic acid with 1-silacyclopent-2-enes **89 - 91** was carried out in the same way as for **88d - P**.[160] The reactions afford the protodeborylated product and the boron compound **142**,[161] the latter was separated from the desired compounds by adopting two methods.



Scheme 7.11. Protodeborylation of 1-silacyclopent-2-enes, **89 - 91**.

(1) All volatile materials were removed under reduced pressure, the mixture was dissolved in pentane (ca. 5 mL). The solution was kept overnight at low temperature (–35 °C). The precipitated compound **142** was separated from the desired product (soluble in pentane). This method failed for the compounds (protodeborylated products) with larger molecular weight which also precipitated out at the same low temperature. The work up procedure was changed and a second method was adopted for the purification of such compounds.

(2) The mixture was heated (80 - 100 °C, 1 - 2 h) under reduced pressure. All the boron-oxygen compound sublimed and its crystals were collected along the walls of the Schlenk tube. The desired compounds remained as oils, were separated and characterized.

Being a reactive group, it was expected that the Si-Cl function will react in the presence of acetic acid and will result in elimination of HCl. Surprisingly, this function survives even in the presence of an excess of acetic acid for 30 - 60 min. The reactions were applied for compounds containing one Si-Cl function as in **89 - P**, **90 - P** as well as for silane bearing two Si-Cl groups, **91a - P**.

NMR spectroscopic studies

The NMR data (^{13}C and ^{29}Si) of protodeborylated 1-silacyclopent-2-enes **89 - P** to **91 - P** are listed in Table 7.10 and the corresponding ^{1}H NMR data are summarized in Experimantal section. The data set is fully consistent with the proposed structures. In ^{13}C NMR spectra, the sharp signal of C-3, previously linked to boron, now shows ^{29}Si coupling satellites (≈ 15 Hz for **89 - P**, **90 - P** and 22.4 Hz for **91 - P**). There is no major change in the rest of the skeleton, and this is also seen in the ^{13}C NMR spectra (Figure 7.11). The ^{29}Si NMR spectra are useful in getting some important information like, ^{13}C satellites including those for ^{13}C-3 (Figure 7.12). In ^{1}H NMR spectra, the signal for proton bonded to C-3 emerges with ^{29}Si satellites for $^{3}J(^{1}H,^{29}Si)$. On the basis of full NMR data the structures were proposed, and the first protodeborylated example (**90c - P**) was studied by X-ray crystallography.

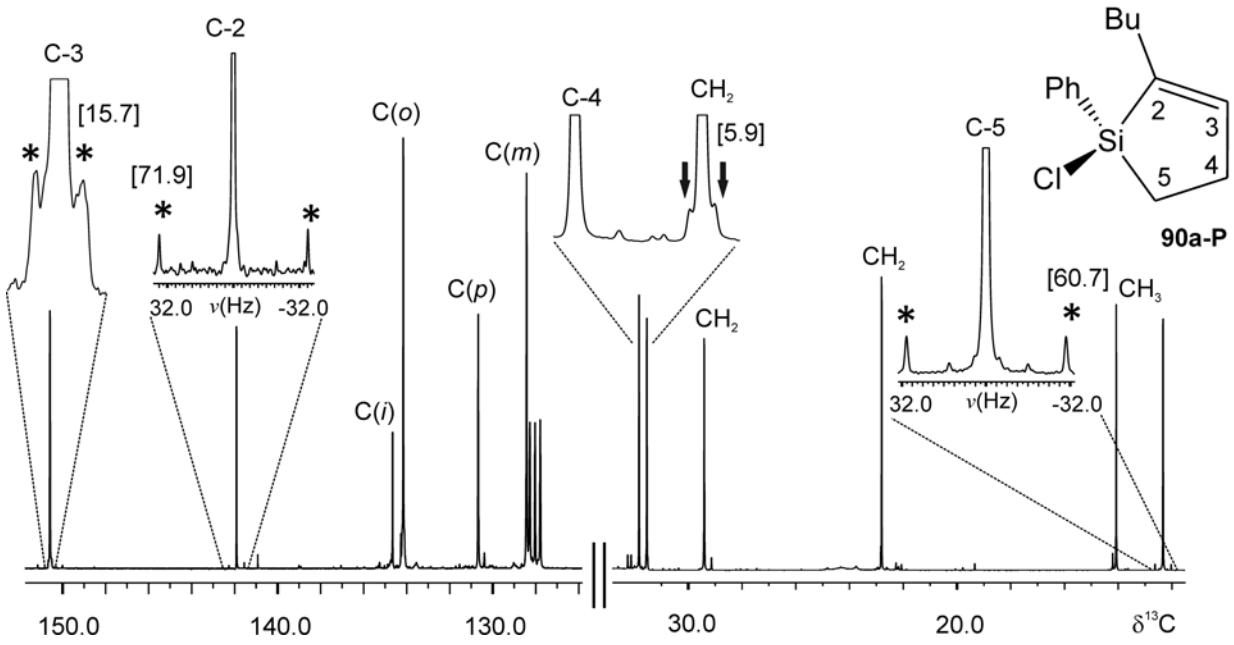


Figure 7.11. 100.5 MHz $^{13}C\{^{1}H\}$ NMR spectra of **90a - P**, ^{29}Si satellites are marked by asterisks in expansions, corresponding to $^{1}J(^{13}C,^{29}Si)$ and $^{2}J(^{13}C,^{29}Si)$.

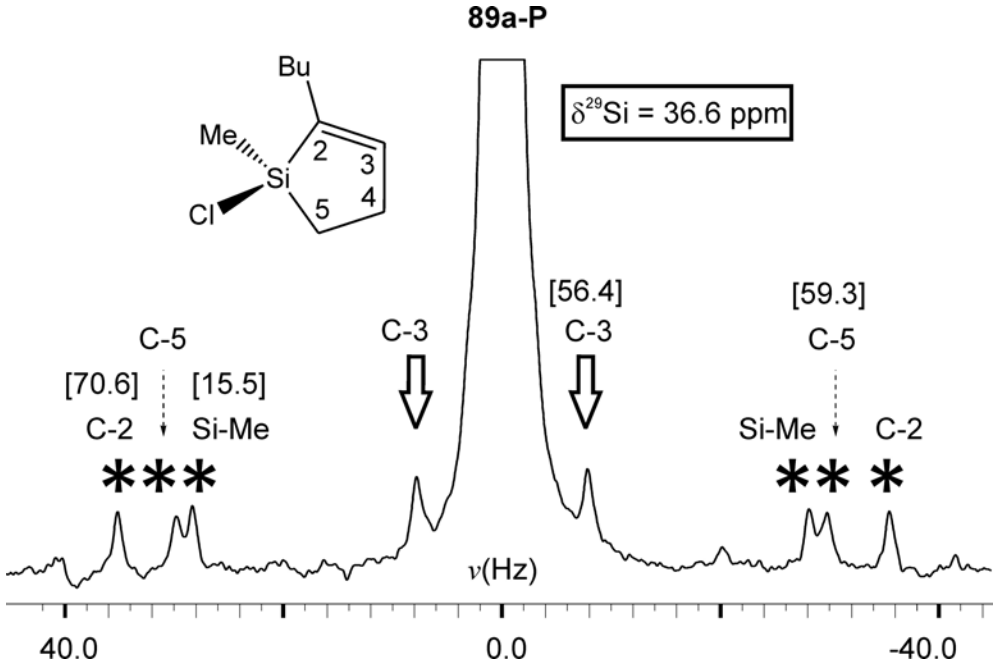


Figure 7.12. 79.6 MHz $^{29}Si\{^{1}H\}$ NMR spectra of **89a - P**, expansion of the parent signal is given. The ^{13}C satellites, marked by asterisks, correspond to $J(^{13}C,^{29}Si)$ The same coupling constants can be confirmed from ^{13}C NMR spectra of **89a - P**.

*X-ray crystallographic analysis of **90c - P***

The molecular structure of **90c - P** is shown in Figure 7.13, selected structural parameters are listed in the caption of the figure. The data pertinent to crystal structure determination are given in Table 7.10. The molecule has one expectedly small endocyclic C-Si-C angle (94.6°), and the other endocyclic angles are within the expected range if compared with the molecular structure of **89c** and two analogous compounds.[68,69] The bonds C1-C2 = 133.8 pm and C2-C3 = 150.3 pm are shorter than the same type of bonds in **89c** (135.7 pm and 153.1 pm, respectively). The elongation of these bonds in the latter case has been explained on the basis of hyperconjugation involving p_z empty orbital of boron and C-Cσ bond.[120,121] Since, the boryl group is absent in **90c - P**, the relevant bonds become shorter.

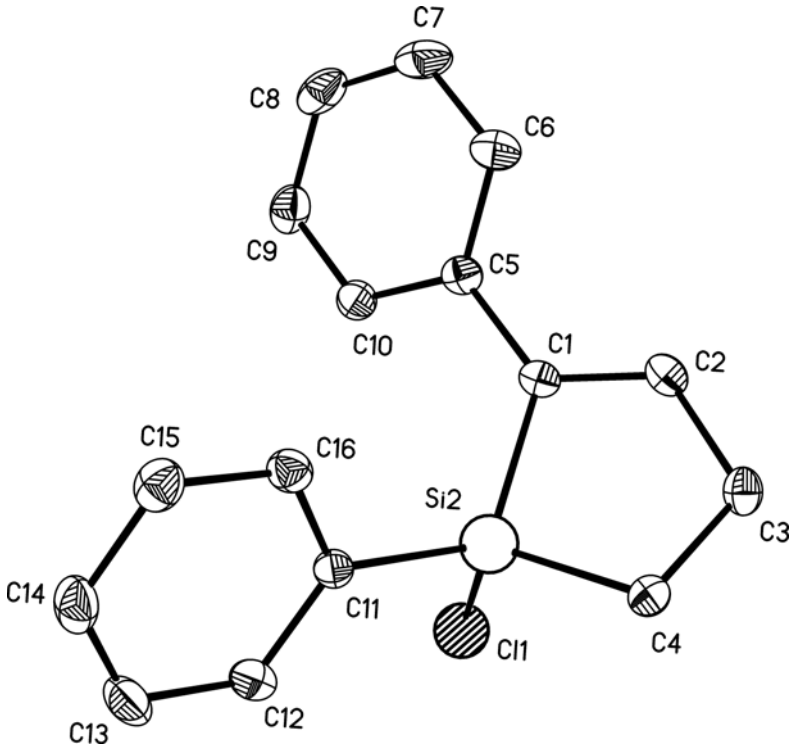
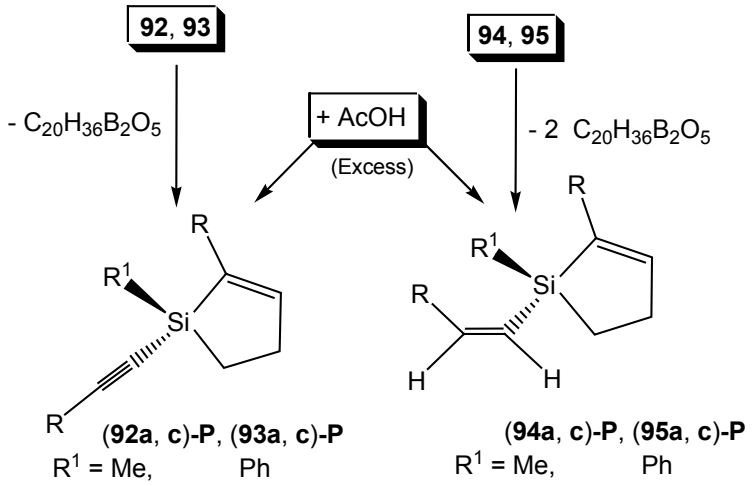


Figure 7.13. Molecular structure of 1-chloro-1,2-diphenyl-1-silacyclopent-2-ene, **90c-P** (ORTEP plot, 40 % probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (pm) and bond angles (deg.): C1-C2 133.8 (2), C1-C5 147.3 (19), C1-Si2 185.1 (14), C2-C3 150.3 (2), C3-C4 154.2 (2), C4-Si2 185.7 (15), C11-Si2 185.4 (15), Si2-Cl1 207.6 (6), C2-C1-C5 124.7 (13), C2-C1-Si2 107.0 (10), C1-C2-C3 120.3 (13), C2-C3-C4 109.6 (12), C4-Si2-Cl1 111.3 (5), C3-C4-Si2 103.7 (10), C16-C11-Si2 119.2 (11), C1-Si2-C11 117.2 (6), C1-Si2-C4 94.6 (7), C1-Si2-Cl1 109.6 (5), C11-Si2-Cl1 105.9 (5).

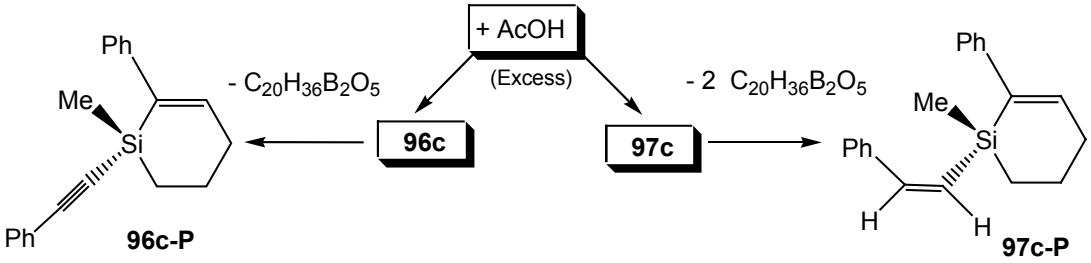
7.4.3. Protodeborylation of 1-alkenyl-, 1-(alkyn-1-yl)-1-silacyclopent-2-enes and 1-(alkyn-1-yl)-1-silacyclohex-2-enes

Protodeborylation of 1-alkenyl-1-silacyclopent-2-ene (**92 - 95**) and 1-silacyclohex-2-ene derivatives (**96** and **97**) were carried out exactly in the same way as for 1-silacyclopent-2-enes (**89 - 91**). The addition of acetic acid to a solution of the respective boryl-substituted silane in pentane or hexane causes the removal of the boryl group. The reactions were carried out at ambient temperature for 30 - 60 min. After removal of all volatile materials the boron compound crystallizes at the bottom of the Schlenk tube at low temperature. Since the starting silanes (boryl-substituted silanes) bear two 9-BBN groups, two equivalents of **142** were formed, and complete removal was not possible just by cooling the reaction mixtures. In order to separate **142** completely, the waxy compounds were heated to 100 °C for 1 - 2 h under reduced pressure. The compound **142** moves slowly up along the walls of the Schlenk tube leaving the oily product behind. Pure samples were obtained (Figure 7.14 and Figure 7.15) as oils and were characterized by multinuclear NMR spectroscopy using C_6D_6 solutions.



Scheme 7.12. Protolysis of 1-(alkyn-1-yl)-1-silacyclopent-2-enes and 1-alkenyl-1-silacyclopent-2-enes.

The exactly analogous procedure was applied for protodeborylation of 1-silacyclohex-2-enes **96c** and **97c**. Both compounds undergo smoothly protodeborylation to afford the products **96c - P** and **97c - P**. These compounds were purified by heating under reduced pressure. When most of **142** was sublimed off, the oily products **96c - P** and **97c - P** were taken up into another Schlenk tube and were characterized by NMR spectroscopy.



Scheme 7.13. Protolysis of 1-(alkyn-1-yl)-1-silacyclohex-2-enes and 1-alkenyl-1-silacyclohex-2-enes.

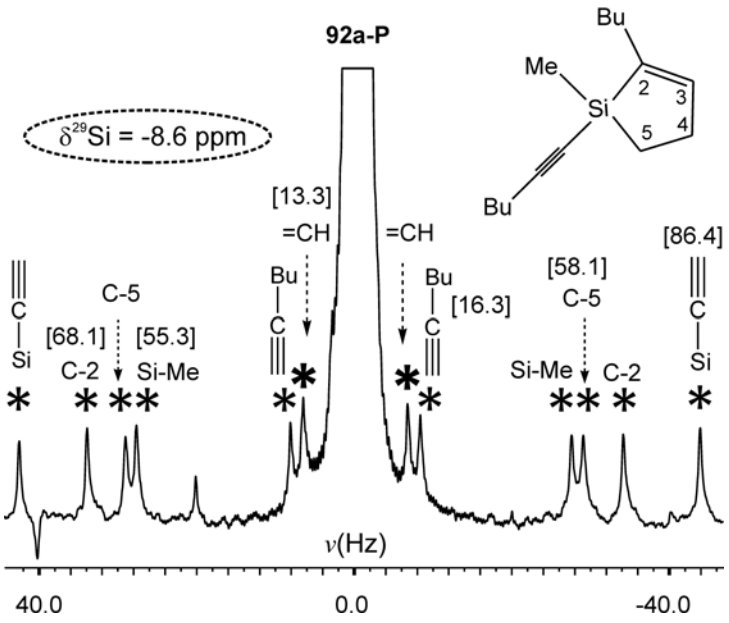


Figure 7.14. ^{29}Si{^{1}H} NMR spectrum (59.57 MHz) of **92a - P**, expansion is given for the parent signal showing ^{13}C satellites, marked by asterisks, corresponding to $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$, coupling constants values are given in brackets.

NMR studies of 1-(alkyn-1-yl)- and 1-alkenyl-1-silacyclopent-2-enes

The NMR data (^{13}C and ^{29}Si) of compounds **92 - P** and **93 - P** are collected in Table 7.11 and those of compounds **94 - P**, **95 - P** in Table 7.12. The ^{1}H NMR data are collected in Experimental part. The data sets (Table 7.11 and Table 7.12) are in close agreement with the proposed structures. All the ^{13}C NMR signals belonging to the five-membered ring carbons are in the same sequence as for simple five-membered deborylated silanes (**89 - P** to **91 - P**). The ^{29}Si satellites aid the assignment, and the respective coupling constants could be confirmed from ^{29}Si spectra (Figure 7.14). The ^{29}Si NMR signal was shifted by 3 to 4 ppm to lower frequency relative to the respective boryl-substituted silanes. In ^{1}H NMR spectra, the

only difference is seen in the olefinic region where a signal at $\delta \approx 7.0$ ppm appears for ^{1}H(C-3).

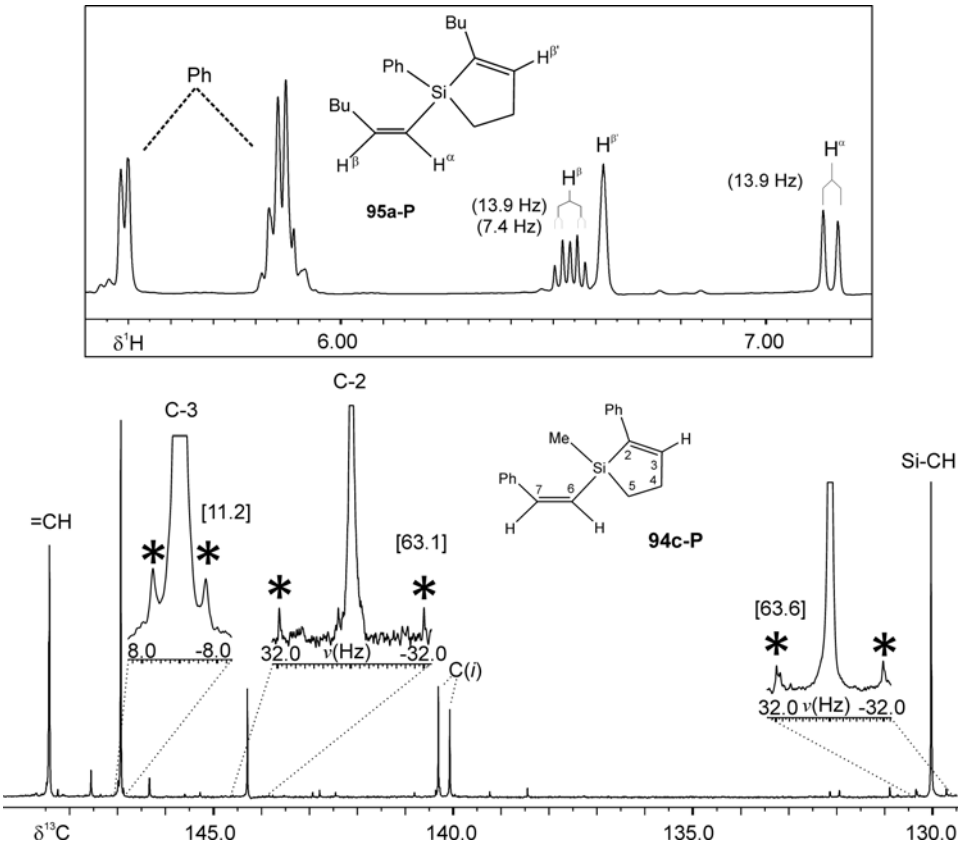


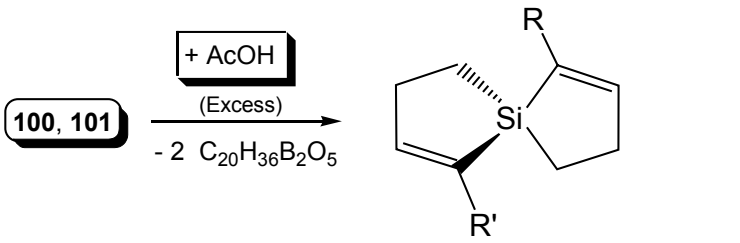
Figure 7.15. Part of ^{13}C{^{1}H} NMR spectra (100.5 MHz) of **94c - P** (lower trace) and ^{1}H (400 MHz) of **95a - P** (upper inserted). Expansions (**94c - P**) are given for signals showing ^{29}Si satellites, marked by asterisks, corresponding to $^{1}J(^{13}C,^{29}Si)$ and $^{2}J(^{13}C,^{29}Si)$.

In the ^{13}C NMR spectra of compounds **94 - P** and **95 - P**, there are expectedly three =^{13}C-H carbons and the respective signals at low field (in the olefinic region; attached proton test NMR) can be seen for all of them. These carbons can be readily identified from their characteristic coupling satellites corresponding to $^{1}J(^{13}C,^{29}Si)$ and $^{2}J(^{13}C,^{29}Si)$. The characteristic chemical shift of these carbons increase the accuracy of assignment. The chemical shifts of C-2 appears $\delta \approx$144 ppm and $\delta \approx$ C-6 at 130 ppm could be clearly distinguished. In contrast the C-3 and C-7 can be distinguished on the basis of $^{2}J(^{13}C,^{29}Si)$ which is well visible for endocyclic C=C bond as compared to the exocyclic one. All other ^{13}C signals (for R and R^{1}) are within the expected range. The multiplicity of ^{1}H NMR signals further supports the structural

assignments. The new C-H bonds appeared as a result of twofold protodeborylation and are marked as α, β and β' (Figure 7.15).

7.4.4. Protodeborylation of spirosilanes

The next target was, to extend the reactions to protodeborylation of spirosilanes and to know whether the same reactions work under the same reaction conditions or not. The spirosilanes **100** and **101** were treated with acetic acid in the same way under mild reaction conditions and afforded smoothly the protodeborylated products **100 - P** and **101 - P**. The boron compound **142** was removed at high temperature (100 - 120 °C) and low pressure. The remaining compounds were oily liquids (**100a - P**) waxy (**100e - P**) or crystalline solids (**100c - P** and **101a - P**). All the products were characterized by multinuclear NMR spectroscopy. A successful attempt was made to get single crystal of **100c - P** suitable for X-ray diffraction and the ever first example was studied by X-ray crystallography.



(**100a**, **c**, **e**, **101a**)**-P**
R = Bu, Ph, 4-^{t}Bu-C_6H_4, Bu
R' = Bu, Ph, 4-^{t}Bu-C_6H_4, 4-^{t}Bu-C_6H_4

Scheme 7.14. Protolysis of boryl-substituted spirosilane derivatives **100** and **101** using acetic acid as protodeborylating reagent.

NMR spectroscopic studies

The NMR data (^{13}C and ^{29}Si) of protodeborylated spirosilane (**100 - P** and **101 - P**) are listed in Table 7.14 and the ^{1}H data are collected in Experimental part. The NMR data fully support the proposed structures. The interpretation of NMR spectra is similar to the compounds discussed above (1-silacyclopent-2-enes **89 - P** to **95 - P**). The same variations in ^{1}H, ^{13}C and ^{29}Si NMR spectra were observed. The disappearance of all carbon signals of 9-BBN and the appearance of a sharp signal of =^{13}CH were the major changes observed in ^{13}C NMR spectra. The respective protons =C^{2,7}H) are also well visible in the ^{1}H NMR spectra. ^{13}C satellite signals representing ^2J(^{13}C(C^{2,7}),^{29}Si) were observed in ^{29}Si NMR spectra (Figure 7.16).

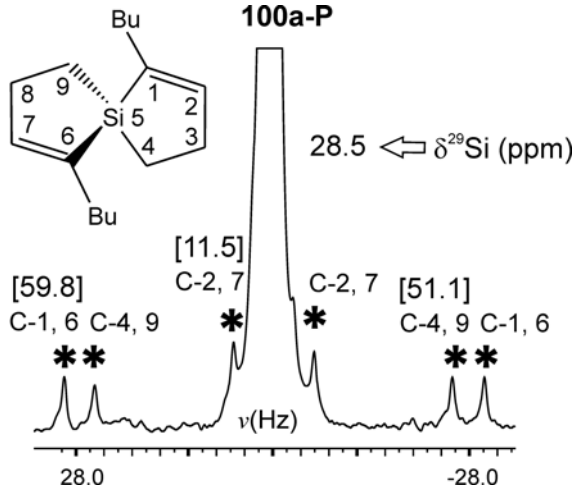


Figure 7.16. $^{29}Si\{^{1}H\}$ NMR (59.6 MHz) spectra of 1,6-dibutyl-5-silaspiro[4.4]nona-1,6-diene **100a - P**. ^{13}C satellites, marked by asterisks, correspond to $^{1}J(^{13}C,^{29}Si)$ and $^{2}J(^{13}C,^{29}Si)$ coupling constants.

*X-ray crystal structural analysis **100c - P***

The spirosilane **100c - P** was crystalline and single crystal suitable for X-ray analysis could be obtained and X-ray diffraction data were collected. The structure is shown in Figure 7.17 together with selected structural parameters. The data related to crystal structure determination and solution are listed in Table 7.15. The ring carbons (C1-4 and C1A-4A) on both sides of the silicon atom are almost in the same plane with mean deviations of 7.2 pm and 4.0 pm, respectively. The five-membered rings are twisted against each other by an angle of 94.1°. The phenyl rings (C5 - 10) and (C5A - 10A) are twisted against their respective five-membered 1-silacyclopent-2-ene rings by 155.1° and 19.4°, respectively. The molecular structure of **100c - P** is well comparable with its immediate precursor **100c**. The changes in most of the bond lengths are either minor or negligible within experimental error. The C2–C3 and C3–C4 bond lengths in **100c - P** are shorter than the respective bonds in **100c** by 2.4 and 1.8 pm, respectively. Elongation of these bonds in **100c** has been attributed to hyperconjugation, involving p_z orbital of boron atom and C-C σ bonds. Moreover, the interatomic distance of C4-Si is longer than the respective bond in **100c** by 1.2 pm. In a similar way all the bond angles of both molecules **100c - P** and **100c** were also compared, and an increase of 3.8° was found in $\angle$ C4-C3-C2 while a decrease in $\angle$ C3-C2-C1 by 1.8° was observed. Intermolecular interactions were negligible.

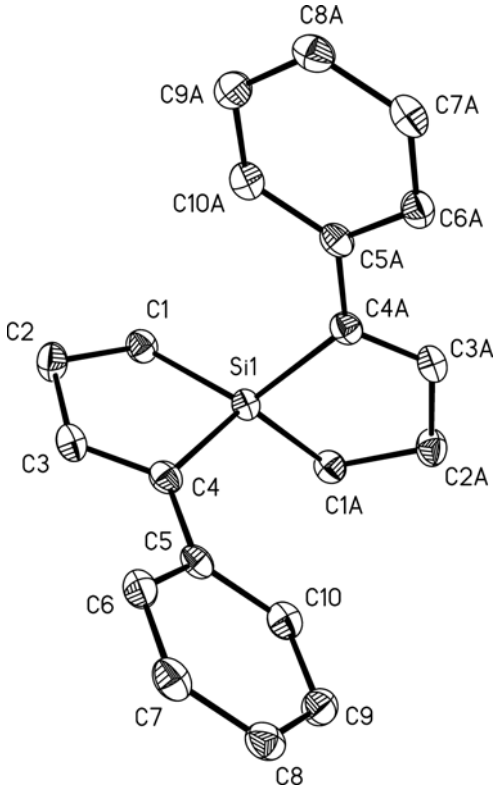


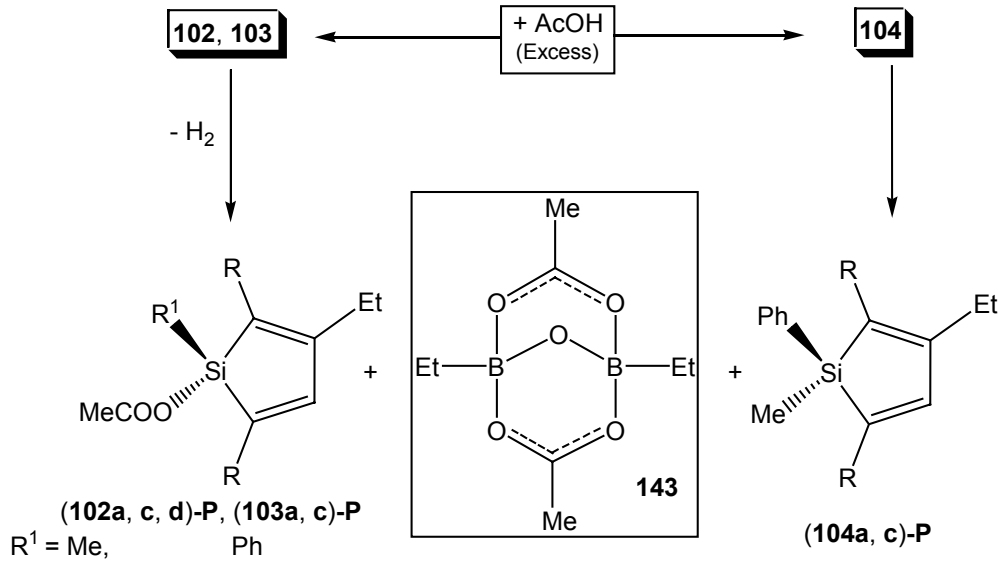
Figure 7.17. Molecuar structure of.1,6-diphenyl-5-silaspiro[4.4]nona-1,6-diene **100c - P**.(ORTEP plot, 40 % probability, Hydrogen atoms are omitted for clarity). Selected bond lengths (pm) and bond angles (deg): C1-C2 154.4 (2), C1-Si1 187.3 (16), C2-C3 150.2 (2), C3-C4 134.0 (2), C4-C5 147.6 (2), C4-Si1 187.9 (16), C2-C1-Si1 105.6 (11), C3-C2-C1 109.8 (13), C4-C3-C2 120.4 (14), C3-C4-C5 124.2 (14), C3-C4-Si1 108.2 (12), C10-C5-C4 120.3 (14), C1-Si1-C4 93.4 (7), C1-Si1-C1 117.2 (11), C4-Si1-C4 113.7 (10).

7.5. Protodeborylation of silole derivatives

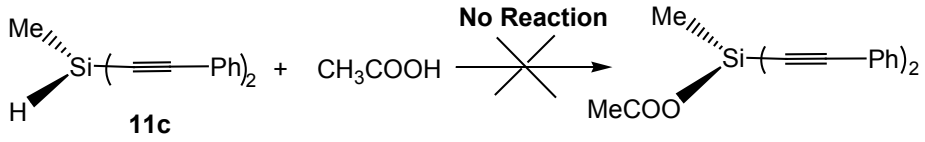
7.5.1. Protodeborylation of simple siloles

The synthesis of siloles *via* 1,1-organoboration had been extensively studied. [29,61,163] The siloles obtained by this way are air and moisture sensitive owing to the presence of the BEt_2 group at C-3. After synthesis of siloles *via* 1,1-organoboration, the next challenge was the substitution of BR_2 group by any insensitive group preferably a hydrogen atom. Several protic reagents such as acetic acid, water and ethanolamine have been studied for protolysis of siloles.[45,59,60,71,78,79] In each report only representative examples have been presented and complete data sets for protodeborylated siloles have not been reported. Moreover, the boron compounds have almost been ignored, especially in the case of acetic acid where no fully

characterized compounds have been reported. The work presented here (Scheme 7.15) was started with the hope to collect solution state NMR data for protodeborylated siloles and also to elucidate the fate of the boron compound formed. The NMR data of the reaction mixture indicated the presence of **143**, already reported and formed in a completely different way.[5] Attempts were made to study most of the compounds for the said conversion and to point out the limitations. Fortunately the protodeborylation reactions proceeded smoothly without any obstacles. The idea of functional groups on silicon atom was still under consideration and the Si-H group was selected for these reactions. The work was focused on the application of acetic acid as protodeborylating reagent. It was expected that the reactions will follow normal routes and hopefully the Si-H function will remain untouched. It was extremely interesting to observe that both the BEt_2 and Si-H groups were simultaneously substituted by hydrogen and acetoxy group, respectively. Attempts were made to understand the effect of various substituents (R = Bu, Ph, 4-Me-C_6H_4, 4-^{t}Bu-C_6H_4 and R^1 = Me, Ph) responsible for making Si-H function more sensitive. The results of all the reactions were identical under identical reaction conditions. The reactivity of Si-H function in the starting silane **11** was studied. The treatment of dialkyn-1-ylsilane **11** (Scheme 7.16) with acetic acid shows no reactivity under identical reaction conditions applied to prodeborylation of siloles and it was concluded that the reactivity of Si-H function is the result of silole ring.



Scheme 7.15. Protolysis of siloles using acetic acid as protic reagent.



Scheme 7.16. Unsuccessful attempt to determine the reactivity of Si-H bond in dialkyn-1-ylsilane with acetic acid at ambient temperature.

Two examples of siloles containing the Si(Ph)Me moiety, **104a** and **104c** were also treated with the same protodeborylated reagent under identical reaction conditions. For these siloles nothing special was observed and the BEt_2 group was smoothly removed in the reaction with an excess of acetic acid.

NMR spectroscopic studies

The NMR data (^{13}C and ^{29}Si) of siloles **102 - P** to **104 - P** are given in Table 7.16 and ^{1}H NMR data in Experimental part. The data sets are consistent with the proposed structures. It is evident from the data that the structures of the deborylated siloles correspond closely to each other. The ^{13}C NMR data are most informative in the olefinic (Figure 7.18) as well as in aliphatic region. A sharp ^{13}C(C-3) NMR signal appears with ^{29}Si satellites for $^{2}J(^{13}C,^{29}Si)$ (≈ 10 Hz), replacing the typically broad ^{13}C(C-3) NMR signal in the respective 3-diethylboryl-substituted siloles. The disappearance of ^{13}C signals of BEt_2 group in aliphatic region also indicates the successful protodeborylation of siloles. The consistent pattern was observed for ^{1}H NMR data. Here, another important change is the disappearance of the ^{1}H(Si-H) NMR signal ($\delta \approx 5$ ppm in the respective starting siloles). The ^{29}Si NMR spectra are useful since the absence iof the Si-H function is readily evident in siloles **102 - P** and **103 - P**, and the introduction of the acetoxy group strongly deshields the silicon nuclei and causing a down field shift (ca. 20 ppm) when compared with the starting siloles. This shift is negligible (1 - 2 ppm) in the siloles **104 - P**, where reaction takes place only at C-3 to remove BEt_2 group from the starting silole **104**. In the ^{29}Si NMR spectra, the ^{13}C satellites for C-3 and C-4 corresponding to $^{2}J(^{13}C,^{29}Si)$ are not resolved owing to the small difference (<1 Hz) in the coupling constant values. The intensity of ^{13}C satellite signals for C-3 and C-4 is almost two times greater than the resolved satellites visible for C-2 and C-5 (Figure 7.19). All other NMR data can be interpreted in the same way as for the 3-diethylboryl-siloles.

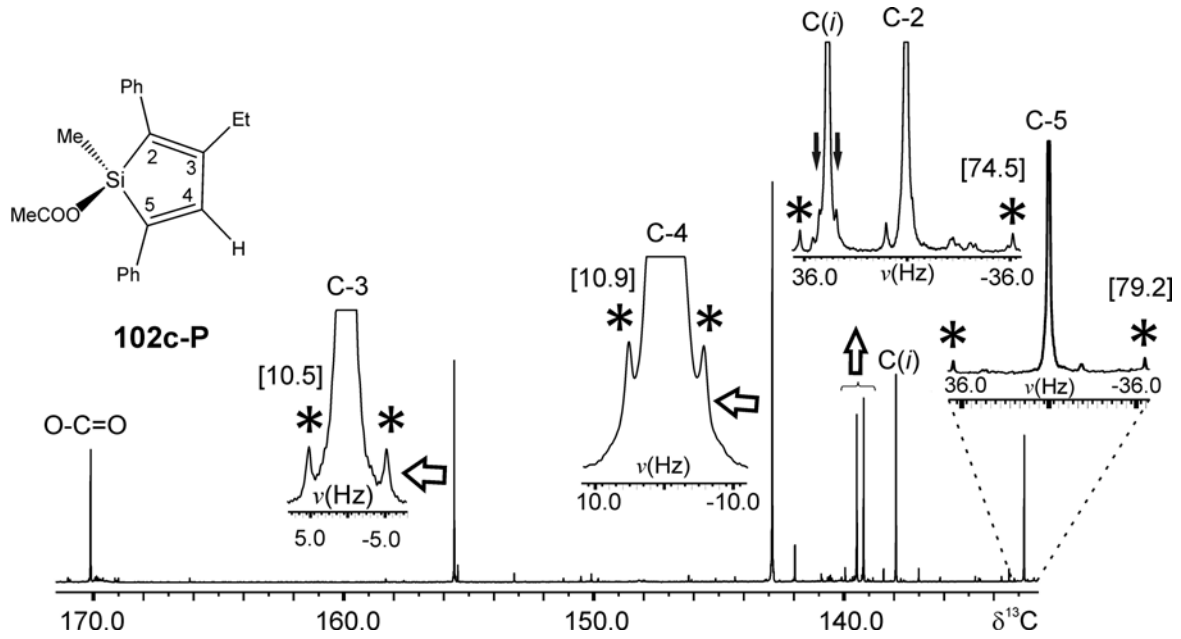


Figure 7.18. Part of $^{13}C\{^{1}H\}$ NMR (100.5 MHz) spectra of **102c - P,** expansions are given for the signals showing $^{1}J(^{13}C,^{29}Si)$ and $^{2}J(^{13}C,^{29}Si)$ spin-spin coupling constants.

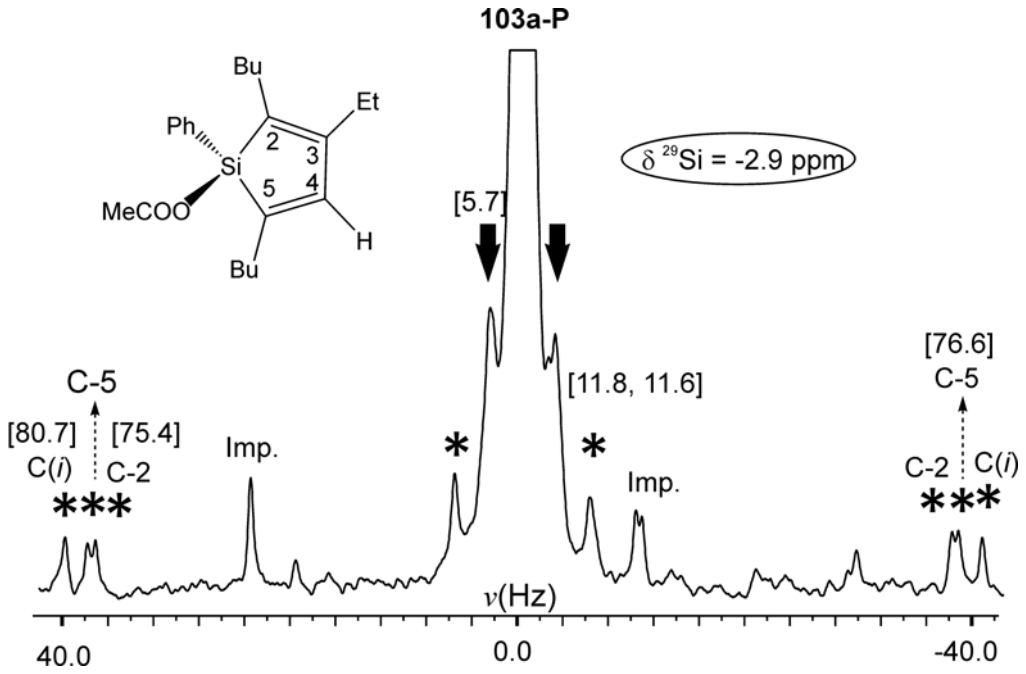
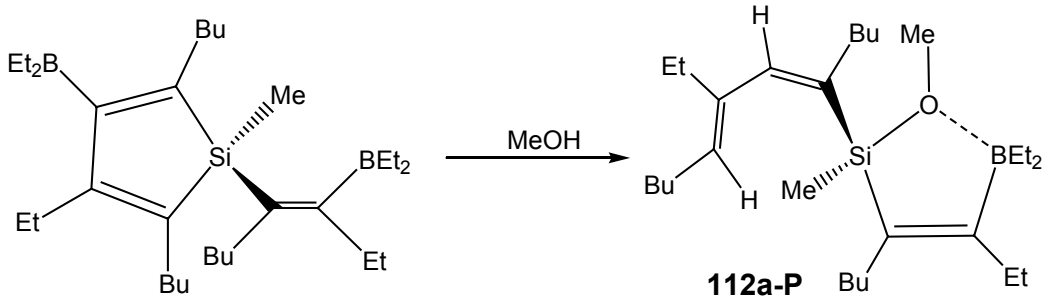


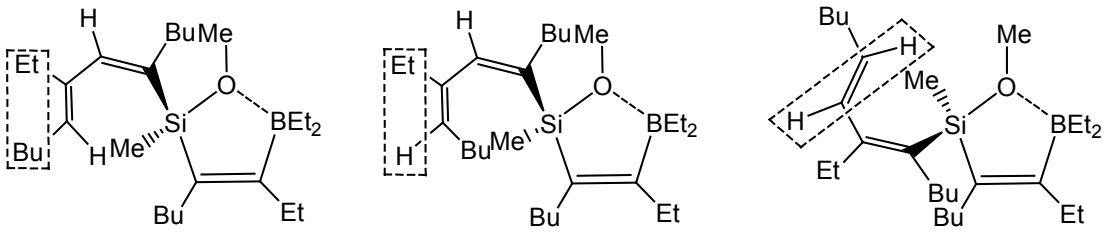
Figure 7.19. Expansion of 79.4 MHz, $^{29}Si\{^{1}H\}$ spectra of **103a - P,** satellites are marked by asterisks. Satellites closed to the parent signals, marked by arrows may arise owing to $^{n}J(^{13}C,^{29}Si)$ coupling constants ($n \geq 2$).

7.5.2. Protodeborylation of 1,1-alkenyl(methyl)silole derivative

The only reaction carried out with a different protic reagent, *i. e.* methanol (MeOH), was the attempted protodeborylation of silole **112a**. A solution of the silole **112a** in hexane was mixed with methanol at room temperature. The starting compound (silole **112a**) possesses two BEt_2 groups. The NMR data indicate that the BEt_2 group from C-3 was removed while the other one remains still in the molecule. The methoxy group attached to this boron atom activates Si-(C-5) bond, causing silole ring opening and at the same time Si-O bond formation. The oxasilaboratole derivatives **112a - P** and **112a - P´** were formed (Scheme 7.17). If the reactivity of both the Si-C bonds (C-2 and C-5) is similar then one would expect two isomers **112a - P** and **112a - P´´** (Scheme 7.18). However, the experimental data reveal that the cleavage of Si-(C-2) is not favoured. This bond appears to be more stable as compared to the Si-(C-5) bond. The cleavage of the former bond would afford the isomer **112a - P´´**, which is unlikely, while the latter affords the isomer **112a - P**, is a favoured product. This statement is supported by ^{1}H NMR data, the isomer **112a - P´´** would give two doublets for protons attached to C-8 and C-9. The experimental data do not contain such signals, indicating that the cleavage of Si-(C-5) bond had occurred. The data contain an additional set which could be tentatively assigned to the isomer **112a - P´** (Figure 7.20 and Table 7.15).



Scheme 7.17. Formation of oxasilaboratole derivative *via* protobeborylation and ring opening of silole **112a**, using MeOH as protic reagent.



Scheme 7.18. Three possible isomers from the reaction of **112a** with MeOH. The isomer **112a - P´´** was not detected in the reaction mixture.

NMR spectroscopic studies

The NMR data of the oxasilaboratoles **112a - P** and **112a - P´** are listed in Table 7.17. The proposed structures are strongly supported by the NMR data set. In the ^{13}C NMR spectra, a broad signal (C-B) at high frequency and larger values for $^{1}J(^{13}C,^{29}Si)$ > 75 Hz, as compared to the silole **112a** are indications of the proposed structures. The $\delta^{11}B$ value at 18.3 ppm is close to the typical region for four-coordinated boron. The $^{1}J(^{13}C,^{29}Si)$ coupling constant values, ^{11}B and ^{29}Si NMR chemical shifts were compared with reported data for analogous oxasilaboratoles and were found to be in close agreement.[164]

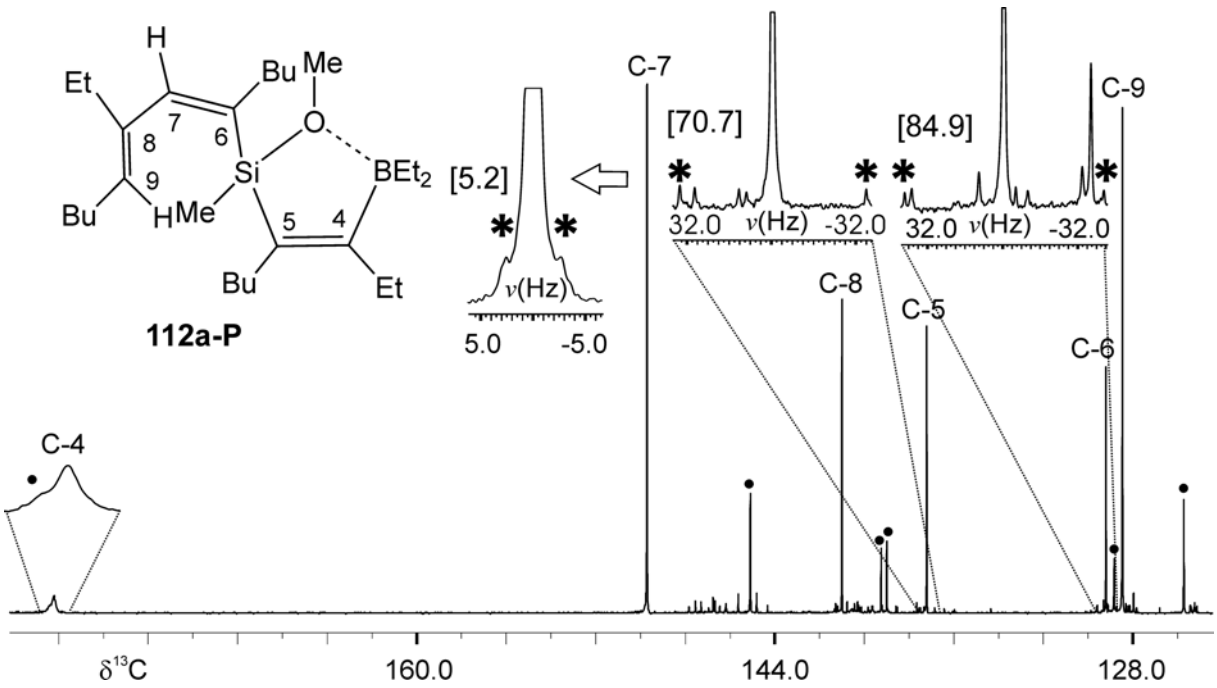
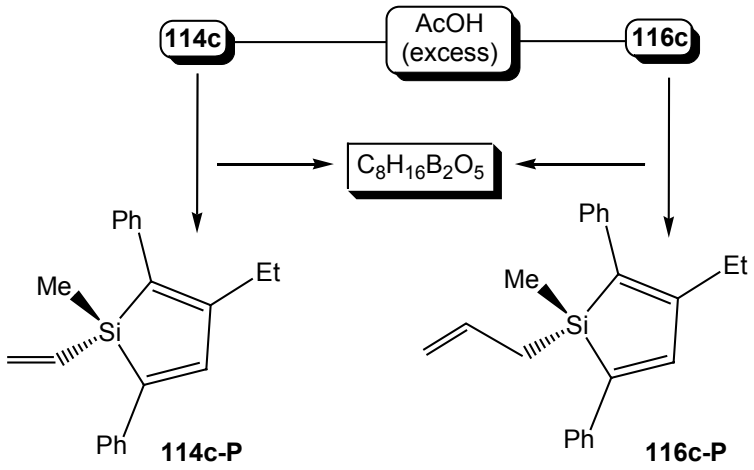


Figure 7.20. Part of 100.4 MHz $^{13}C\{^{1}H\}$ NMR spectrum of the oxasilaboratole **112a - P**. A considerable amount of second isomer present is marked by circles and the ^{29}Si satellites for the major isomer, marked by asterisks. correspond to $^{1}J(^{13}C,^{29}Si)$ and $^{2}J(^{13}C,^{29}Si)$ couplings.

7.5.3. Protodeborylation of 1-vinyl- and 1-allylsiloles

Two examples of siloles bearing Si-vinyl and Si-allyl functional groups were studied with respect to protodeborylation. The principle aim behind these reactions was to extend the scope of deborylation reactions to most of the siloles synthesised in this work. The silole **114c** and **116c** were treated with acetic acid and protodeborylated siloles were obtained (Scheme 7.19).



Scheme 7.19. Protodeborylation of siloles bearing Si-vinyl and Si-allyl functional groups.

NMR spectroscopic studies

The NMR data of the two representative examples are listed in Table 7.18 and the corresponding ^{1}H NMR data can be found in Experimental part. The NMR data can be interpreted in the same way as discussed for other siloles (*e. g.* **102 - p** to **104 - P**). Regarding the differences in the chemical shifts between products and staring siloles, the ^{29}Si NMR spectra are less informative, since the change is not significant. But all the important coupling constant satellites can be seen and measured form such spectra (Figure 7.21). The structural assignments of the new products were also based on ^{13}C(C-4) and ^{1}H(H-C-4) NMR signals.

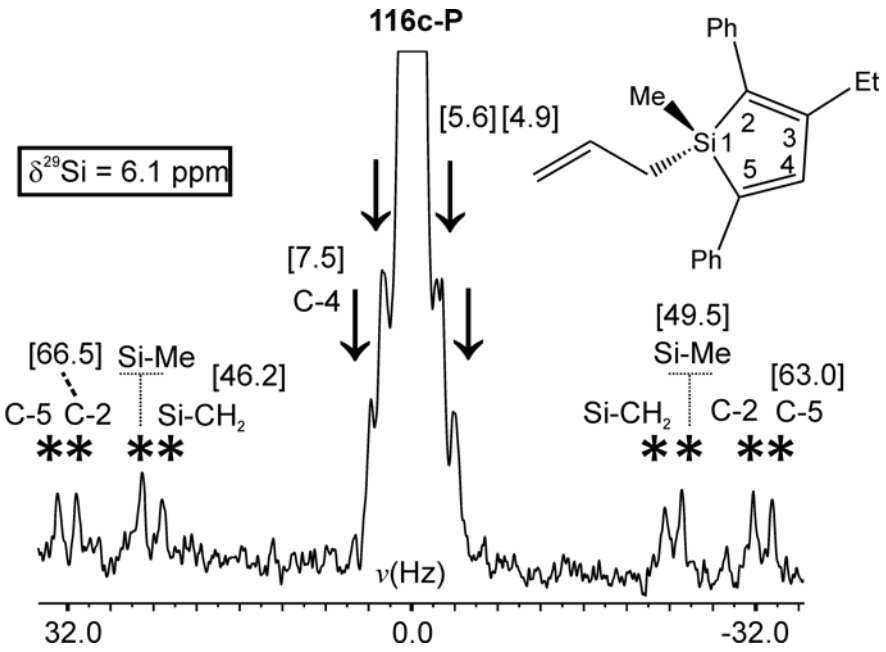
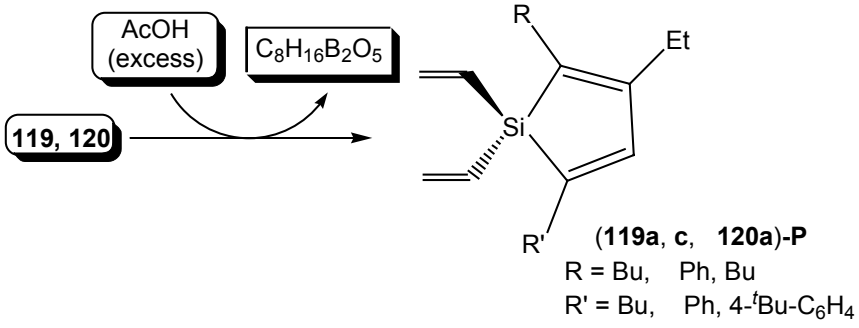


Figure 7.21. 59.6 MHz $^{29}Si\{^{1}H\}$ NMR spectrum of 1-allyl-silole **116c - P**. The ^{13}C satellites for $^{n}J(^{13}C,^{29}Si)$ (n = 1) are marked by asterisks. ^{13}C satellites close to the parent signal (arrows) may be assigned to $^{n}J(^{13}C,^{29}Si)$ (n ≥ 2).

7.5.4. Protodeborylation of 1,1-divinylsiloles

Siloles with vinyl groups on the silicon atom are not known so far. These siloles were not only synthesized *via* 1,1-ethylboration but also the BEt_2 group was successfully replaced by the hydrogen atom (Scheme 7.20). The reaction procedure used for protodeborylation of siloles **102** to **104** was followed to prepare the 1,1-divinylsilole derivatives **119 - P** and **120 - P** in high yield (75 - 80 % from NMR data). The boron-oxygen compound **143** was separated and the siloles, obtained as oily liquids, were characterized on the basis of NMR data.



Scheme 7.20. Treatment of 2,5-dialkyl-3-diethylboryl-4-ethyl-1,1-divinylsilole **119**, **120** with acetic acid to afford 2,5-dialkyl-4-ethyl-1,1-divinylsilole derivatives **119 - P** and **120 - P**.

NMR spectroscopic studies

The NMR data (^{13}C, ^{29}Si and ^{1}H) of 1,1-divinylsiloles (**119 - P** and **120 - P**) are listed in Table 7.19 and Experimental part, respectively. The data set is consistent with the proposed structures. All $J(^{13}C,^{29}Si)$ and $J(^{1}H,^{29}Si)$ spin-spin coupling constant values are in close agreement with the structures studied for analogous siloles so far. All the ^{13}C NMR signals can be assigned unabiguously (Figure 7.22).

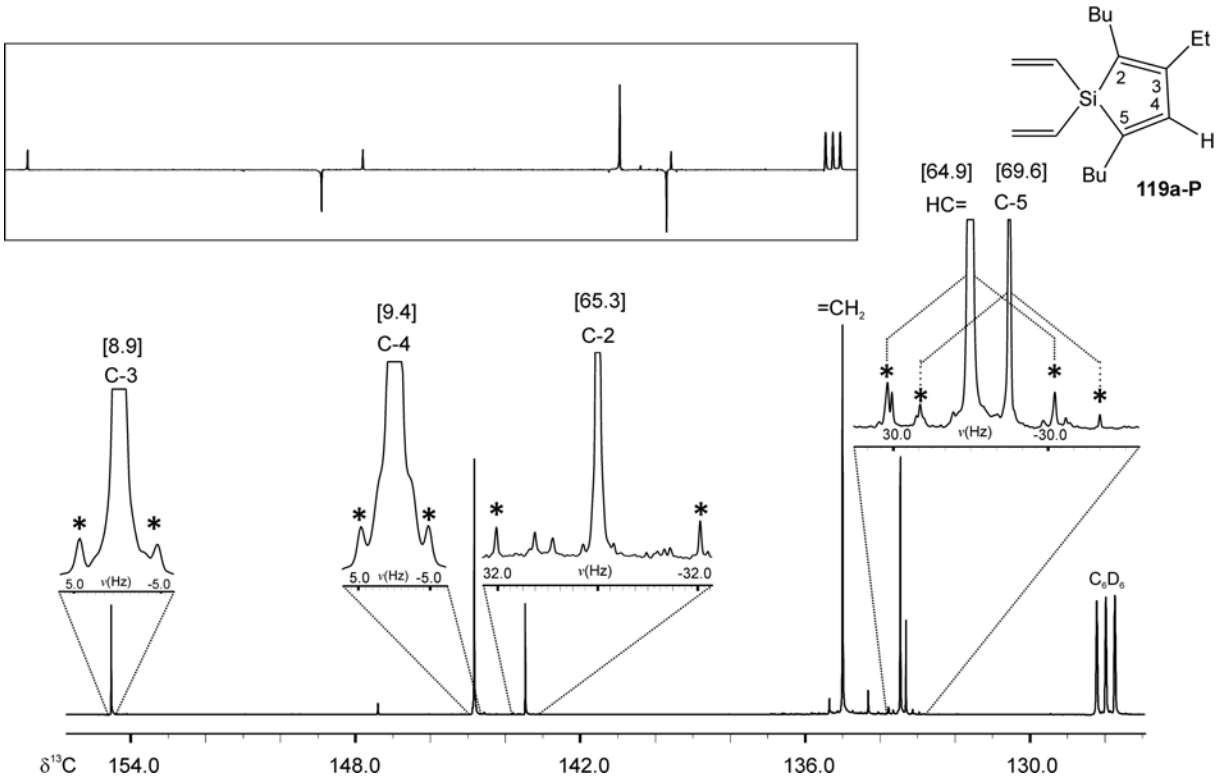
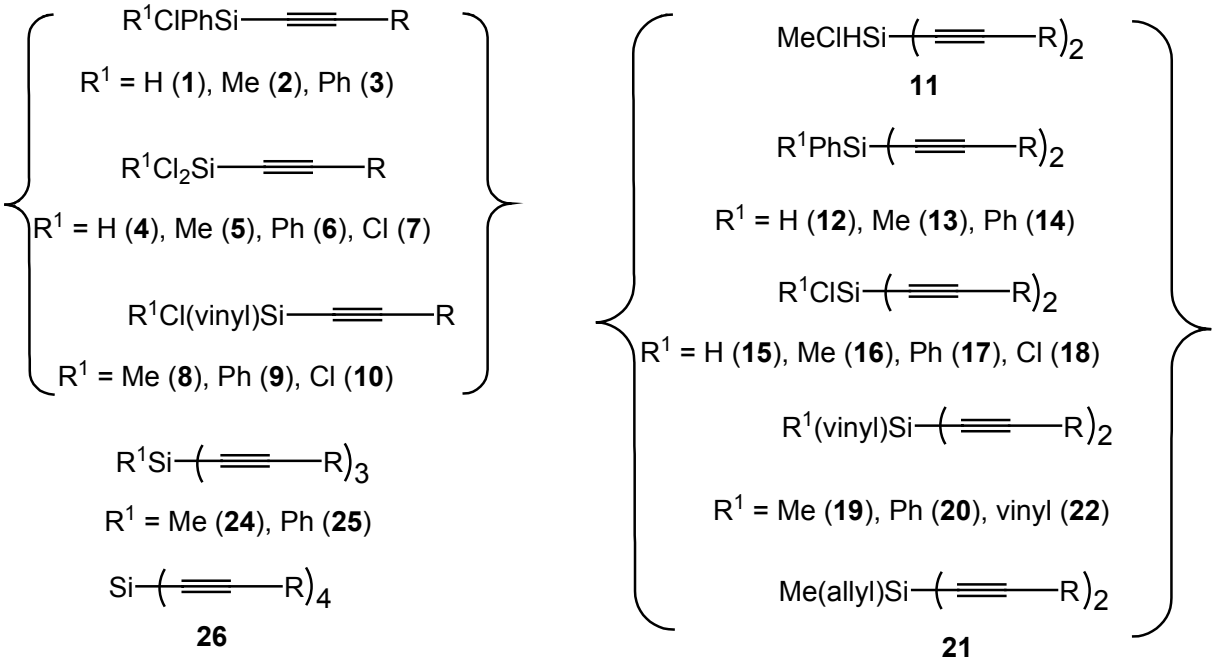


Figure 7.22. Part of $^{13}C\{^{1}H\}$ NMR (100.5 MHz) spectra of 2,5-dibutyl-3-ethyl-1,1-divinylsilole **119a - P**. ^{29}Si satellites, marked by asterisks in expansions, correspond to $^{1}J(^{13}C,^{29}Si)$ and $^{2}J(^{13}C,^{29}Si)$. The upper insert shows the J-modulated ^{13}C NMR spectrum of the same region.

8. SUMMARY

In the course of this dissertation, new alkyn-1-ylsilanes were prepared, characterized and their use in 1,2-hydroboration, 1,1-organoboration reactions or combination of these was demonstrated.

Although the silanes (Scheme 8.1) were in general obtained as mixtures, they could be purified by the conventional methods such as fractional distillation or crystallization (Figure 8.1 and Figure 8.2). Many of these silanes were fully characterized for the first time by modern NMR spectroscopic techniques and in some cases by X-ray structural analysis.



Scheme 8.1. Starting silanes used in various transformations.

The monoalkyn-1-yl(chloro)silanes were treated with BEt_3 at 100 - 120 °C for prolonged periods of time (up to 30 days) and their further reactivities were exploited. For the first time the 1,2-hydroborating behaviour of BEt_3 was discovered in a series of reactions. The silanes containing two or more than two (up to four) alkyn-1-yl groups were used for syntheses of different heterocyclic systems *e. g.* 1-silacyclobutenes, 1-silacyclopent-2-enes, siloles and borolenes etc. Intermediates, if possible, and final products were studied by multinuclear NMR spectroscopy (^{1}H, ^{11}B, ^{13}C, ^{29}Si and ^{119}Sn). Numerous molecular structures were determined by X-ray structural analysis.

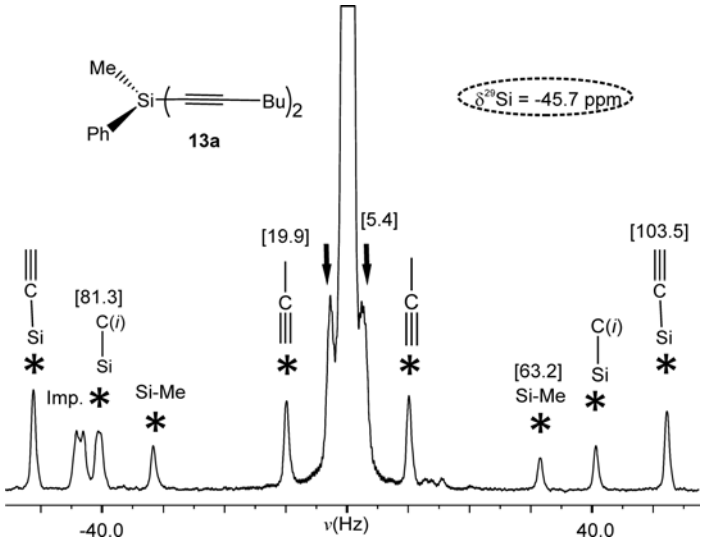


Figure 8.1. 59.6 MHz $^{29}Si\{^{1}H\}$ NMR spectrum of silane **13a**.

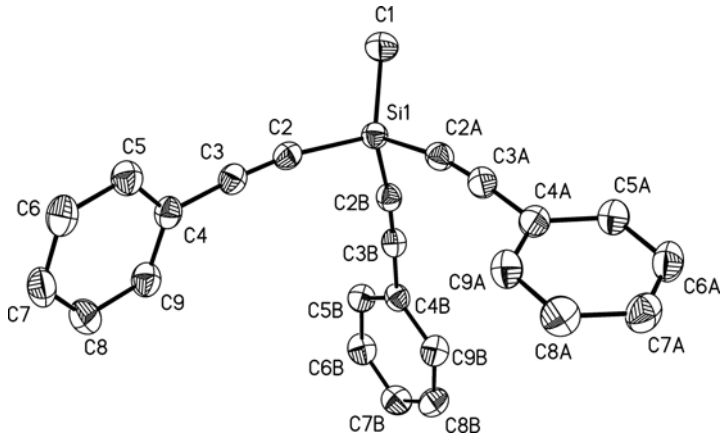


Figure 8.2. Molecular structure of methyl(triphenylethynyl)silane **24c.**

The silanes **1 - 26** give completely different types of new compounds by 1,2-hydroboration and 1,1-organoboration. Reactions of monoalkyn-1-ylsilanes **1 - 7** afford selectively the alkenes (Figure 8.3 and Figure 8.4) on treatment with BEt_3 and 9-BBN. For the first time it was observed that BEt_3 can also act as 1,2-hydroborating reagent if treated with alkyn-1-yl(trichloro)silanes or alkyn-1-yl(dichloro)silanes (**4 - 7**). The same behaviour of BEt_3 was observed with dichloro(vinyl)silane **10**. Thermal 1,2-dehydroboration of BEt_3 had never been observed so far. However in the reactions of BEt_3 with appropriate silanes, 1,2-hydroboration occurred, and a mechanism involving β-hydrogen transfer was proposed. The structures of hydroboration products were confirmed by a consistent set of NMR data (Figure 8.3) together with

some examples in solid state by X-ray crystallography (Figure 8.4, **37c** an example, where 9-BBN has been used for comparison).

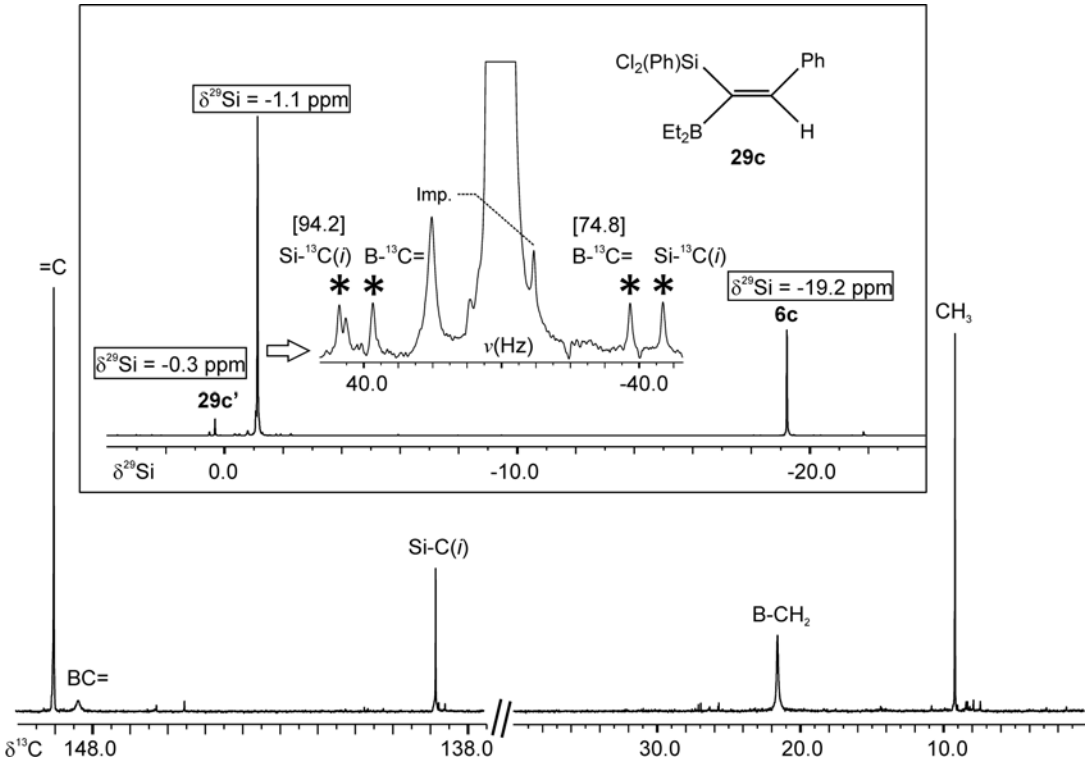


Figure 8.3. 100.5 MHz $^{13}C\{^1H\}$ NMR spectrum of **29c**. Insert: $^{29}Si\{^1H\}$ NMR spectrum (refocused INEPT) of the reaction solution containing the alkene **29c**, starting silane dichloro(phenyl)(phenylethynyl)silane **6c** along with a small amount of the (*E*)-isomer **29c´**.

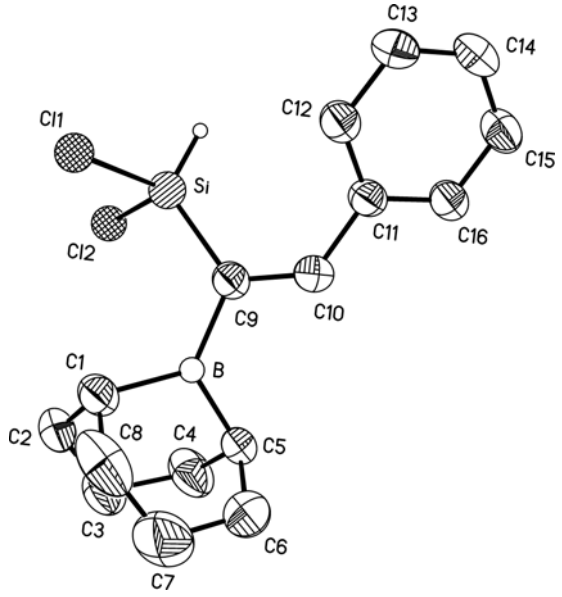
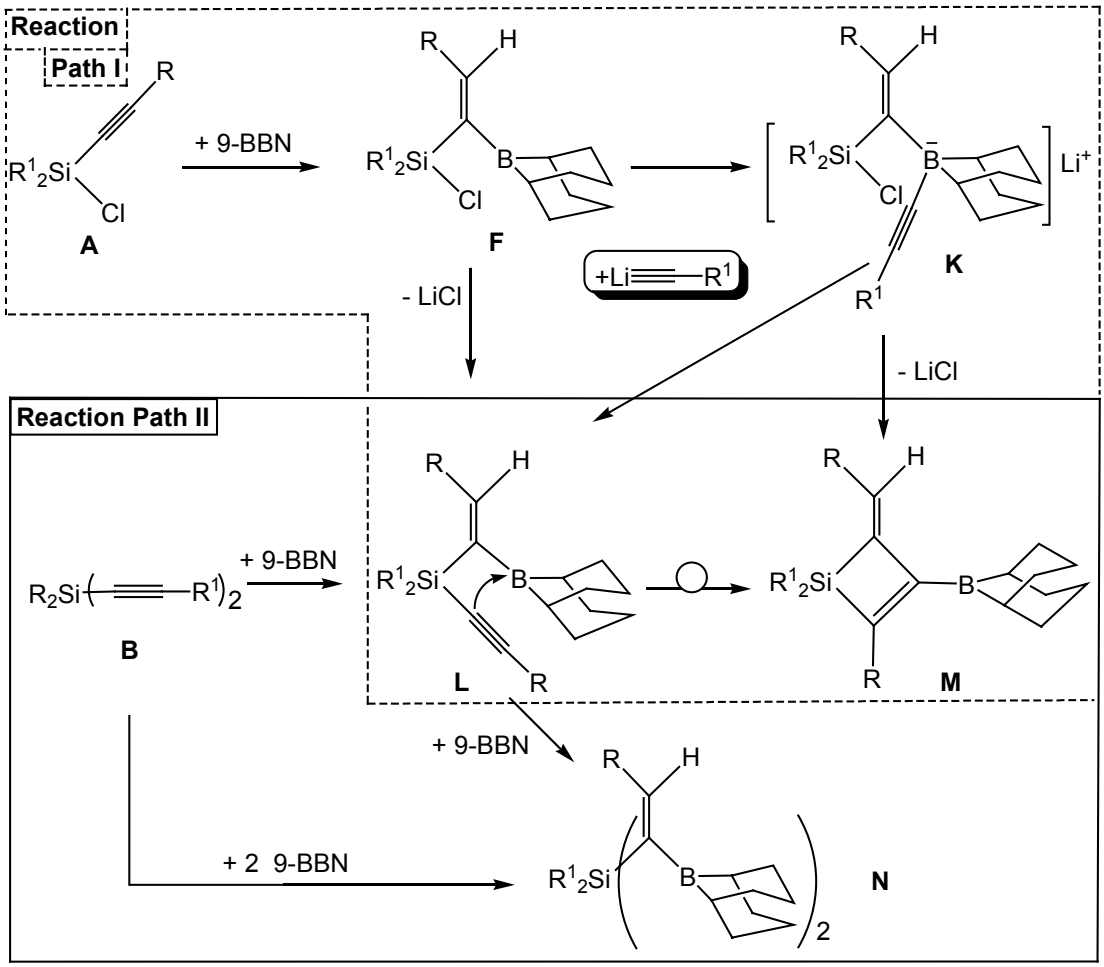


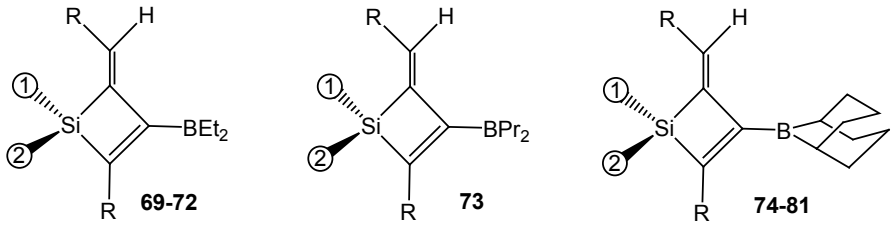
Figure 8.4. Molecular structure of alkenylsilanes **37c**.

These alkenes are useful precursors for further transformations since the silicon atom bears still one or more reactive groups (Si-Cl). They were converted into 1-silacyclobutene derivatives. The reactions proceed *via* an alkyn-1-ylsilane (**L**) or a borate-like zwitterionic intermediate (**K**). Borate intermediates convert slowly into alkyn-1-ylsilane (**L**) at room temperature and afterwards into 1-silacyclobutene (**M**) at elevated temperature 80 - 100 °C. An alternative method was adopted for the syntheses of the desired 1-silacyclobutene derivatives. The dialkyn-1-ylsilanes, **11 - 18** were treated with 9-BBN at 80 - 100 °C, first an alkenyl(alkyn-1-yl)silanes as **L** is formed followed by intramolecular 1,1-vinylboration at the same temperature to afford **M**. The molecular structure of one example (**80a**, Figure 8.5) was determined by X-ray structural analysis.



Scheme 8.2. Syntheses of 1-silacyclobutene derivatives by two different ways, showing the reaction mechanism.

Triorganoboranes such as BEt_3 and BPr_3 afforded 1-silacyclobutenes (Scheme 8.3) on treatment with appropriate dialkyn-1-ylsilanes bearing Si-Cl and $SiCl_2$ groups. This is the result of a rare combination of 1,2-hydroboration and 1,1-organoboration, without using a boron-hydrogen compound.



Scheme 8.3. General formula of 1-silacyclobutenes synthesized in this work. The substituents on Si (1 and 2) as well as R groups have been explained for respective heterocycles.

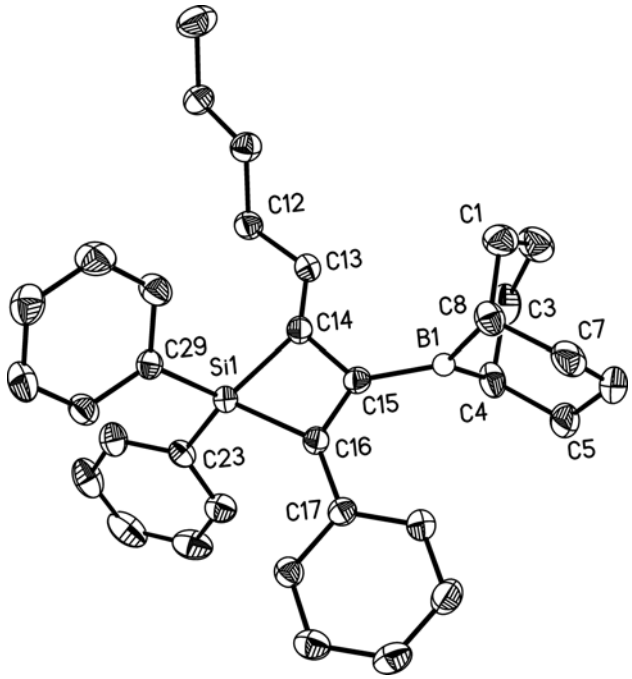
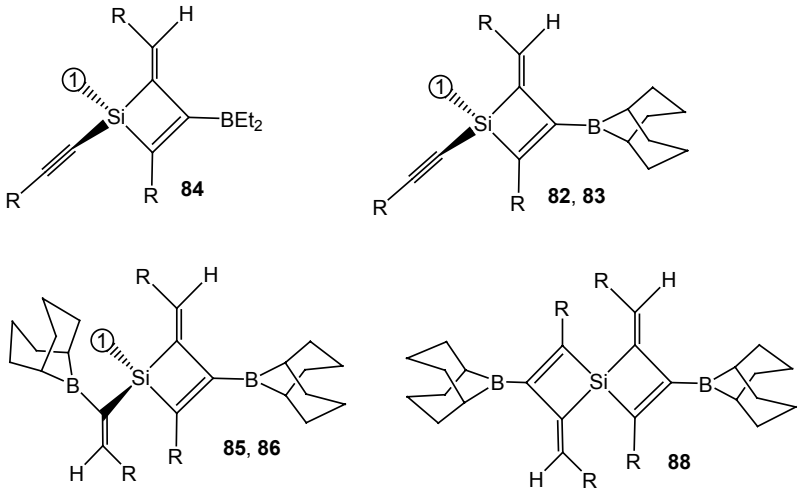


Figure 8.5. Molecular structure of the 1-silacyclobutene derivative **80a.**

Silanes **24** and **25** were reacted with one equivalent and two equivalents of 9-BBN at 80 - 100 °C to afford the 1-silacyclobutene derivatives **82 - 86**. The reactions of silane **26** derivatives with two equivalents of 9-BBN afford spirosilane derivatives **88**. The first example of a molecular structure of such a spirosilane was determined for **88d** by X-ray crystallography (Figure 8.6).



Scheme 8.4. 1-Silacyclobutene derivatives including spirosilanes.

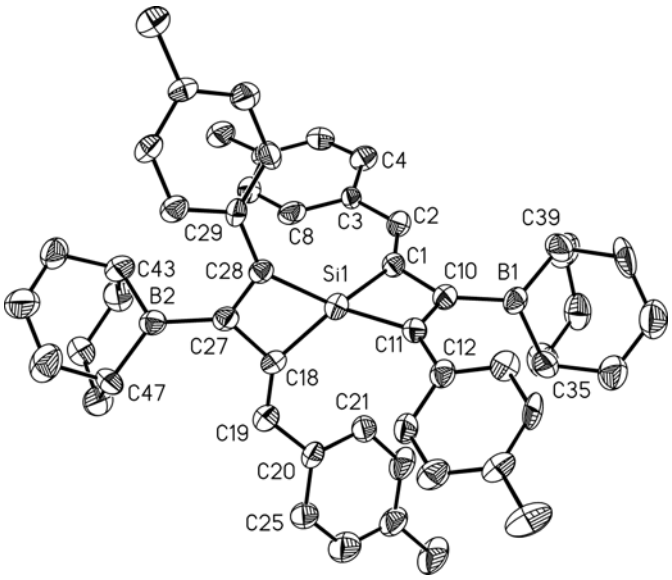


Figure 8.6. Molecular structure of spirosilane **88d**.

The reactions of alkyn-1-yl(vinyl)silanes **8** - **10**, **19**, **20** and **21** with 9-BBN show that 9-BBN prefer the terminal $CH=CH_2$ over the -C≡C- group for 1,2-hydroboration and ring closure by 1,1-organoboration leads to the 1-silacyclopent-2-ene derivatives **89** - **95** and 1-silacyclohex-2-enes **96** and **97**, respectively. For the first time, a molecular structure of a 1-silacyclopent-2-ene bearing the Si-Cl function was determined by X-ray analysis (Figure 8.7).

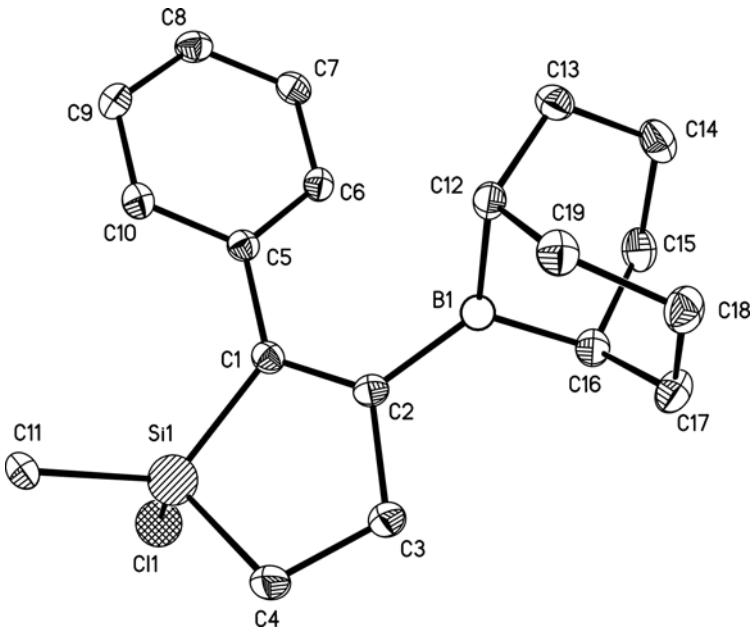


Figure 8.7. Structural representation of 2-(9-borabicyclo[3.3.1]nonyl)-1-chloro-1-methyl-2-phenyl-1-silacyclopent-2-ene **89c**.

Dialkyn-1-yl(divinyl)silanes should give spirosilanes on reaction with two equivalents of 9-BBN. The formation of such spirosilanes was studied in solution and one molecular structure for **100c** was determined by X-ray analysis (Figure 8.8).

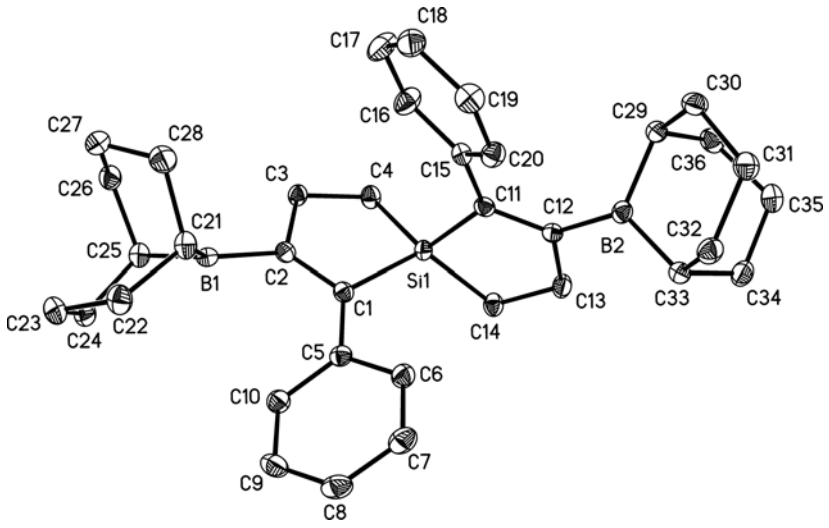


Figure 8.8. Molecular structure of 2,7-bis[9-(9-borabicyclo[3.3.1]nonyl)]-1,6-diphenyl-5-silaspiro[4.4]nona-1,6-diene **100c**.

The silacyclopent-2-ene and silacyclohex-2-ene derivatives including spirosilanes were used in protodeborylation reactions. They react at 23 °C with acetic acid in

non-polar solvents (pentane, hexane or toluene) to afford the respective protodeborylated products. The boron-oxygen compound **142** was detected in solutions, isolated and studied by X-ray structural analysis (Figure 8.9).

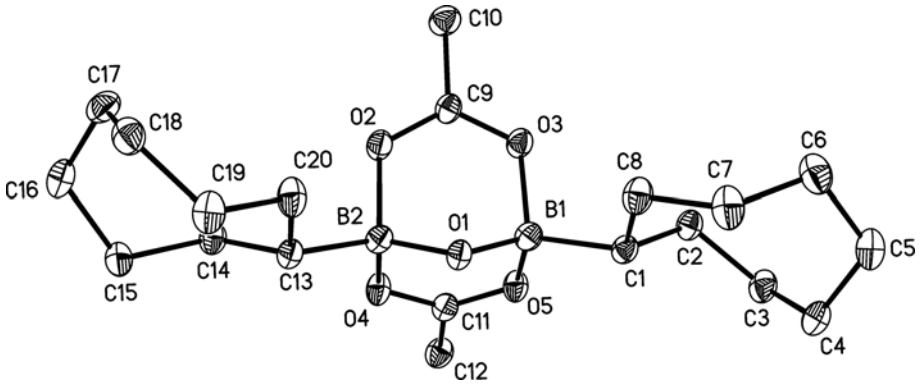


Figure 8.9. Molecular structure of the boron-oxygen bicyclic compound **142**.

All the protodeborylated products were obtained as oily liquids or crystalline materials. The molecular structures for 1-silacyclopent-2-ene **90c - P** and the spirosilane **100c - P** were determined by X-ray analysis (Figure 8.10 and Figure 8. 11).

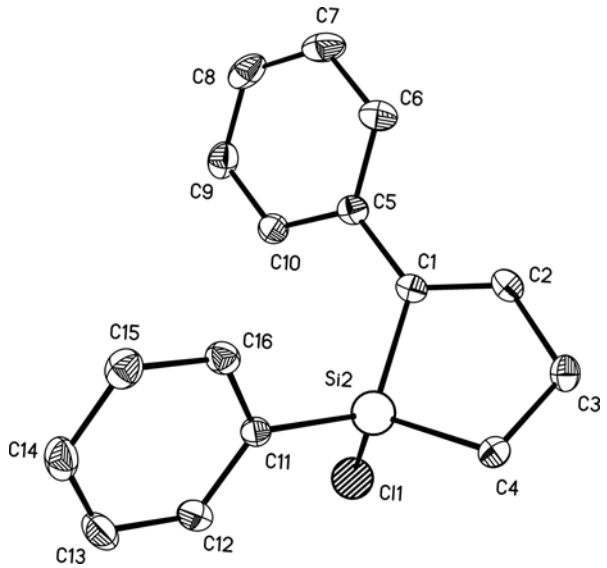


Figure 8.10. Structure of 1-chloro-1,2-diphenyl-1-silacyclopent-2-ene **90c - P**.

Many dialkynylsilanes react with BEt_3 under harsh reaction conditions (at 100 - 120 °C for several days) to afford siloles as the result of 1,1-ethylboration followed by 1,1-vinylboration. The method is very useful and fairly pure siloles were isolated (Scheme 8.5). Their synthetic potential was explored. The Et_2B group was removed

with acetic acid in almost all cases at ambient temperature. It was observed that Si-H function can not tolerate acetic acid, allowing for introduction of -Si-OAc group to the respective silole ring (Scheme 8.5).

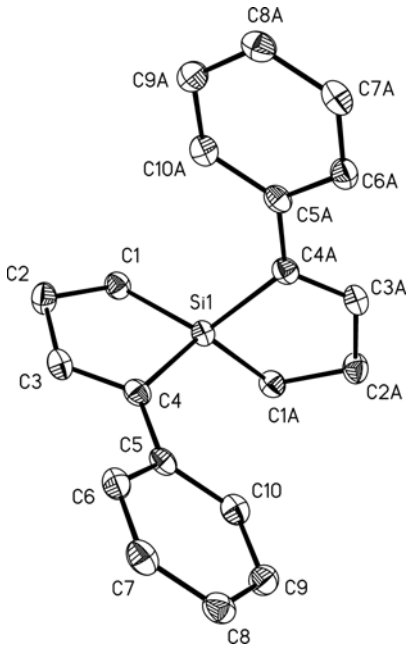
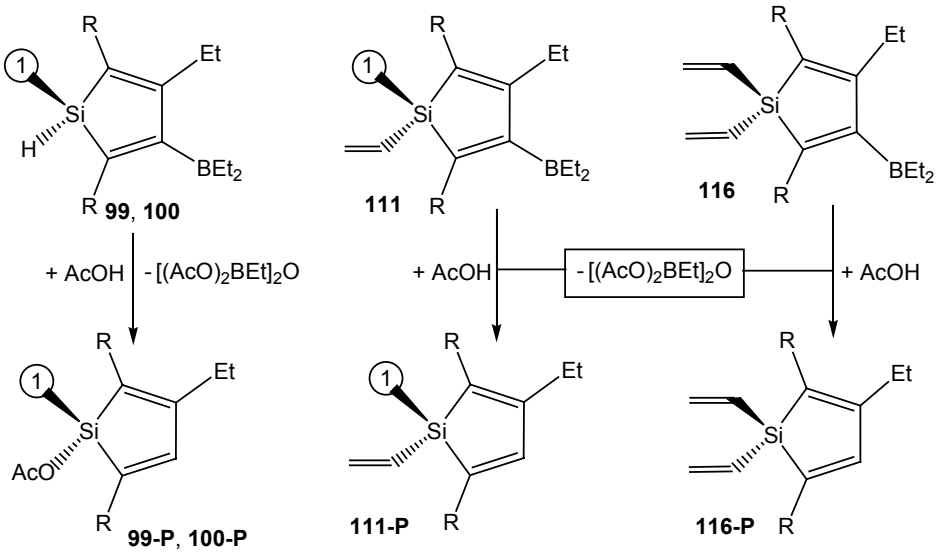


Figure 8. 11. Structure of 1,6-diphenyl-1-silaspiro[4.4]nona-1,6-diene **100c - P**.



Scheme 8.5. Representative examples of siloles.

The treatment of **12c** with 9-ethyl-9-borabicyclo[3.3.1]nonane affords silole **109c** as crystalline material suitable for X-ray structural analysis. This is the first example of a molecular structure of a silole obtained by 1,1-organoboration (Figure 8.12).

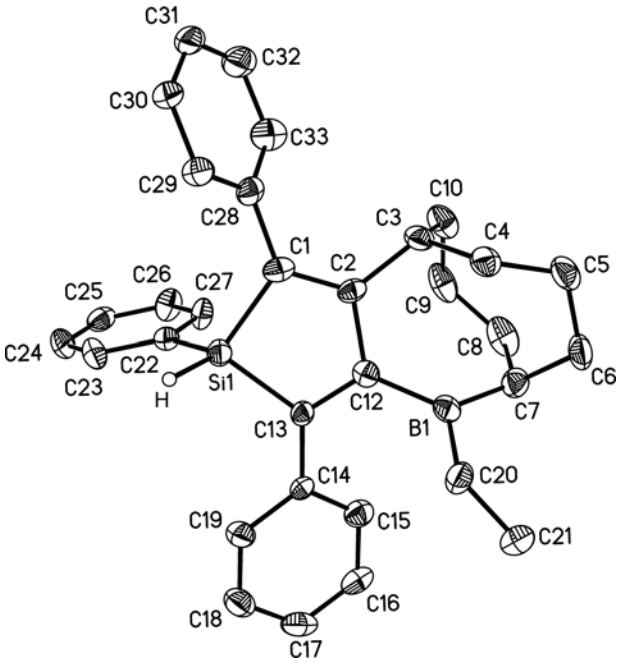


Figure 8.12. Molecular structure of the silole **109c**

By studying the reactivity of the Si-Cl function and the behaviour of the alkenylsilane **35c** or **36c**, with various reagents, crystalline materials could be obtained for determining molecular structures of the novel heterocycles **121** and **123** (Figure 8. 13 and Figure 8.14) and 9-hydroxy-9-borabicyclo[3.3.1]nonane **122**.

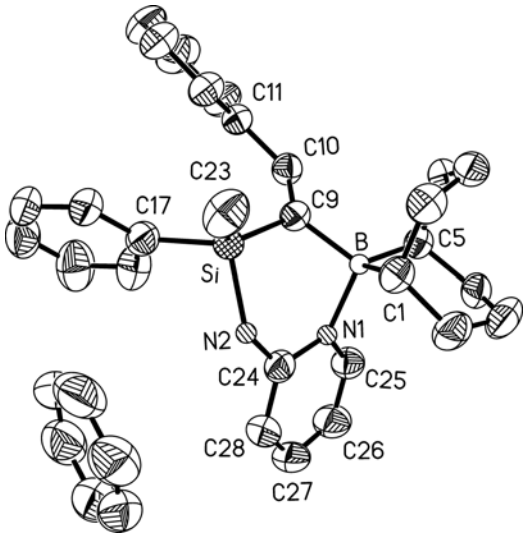


Figure 8. 13. Molecular structure of the heteropolycycle **121**.

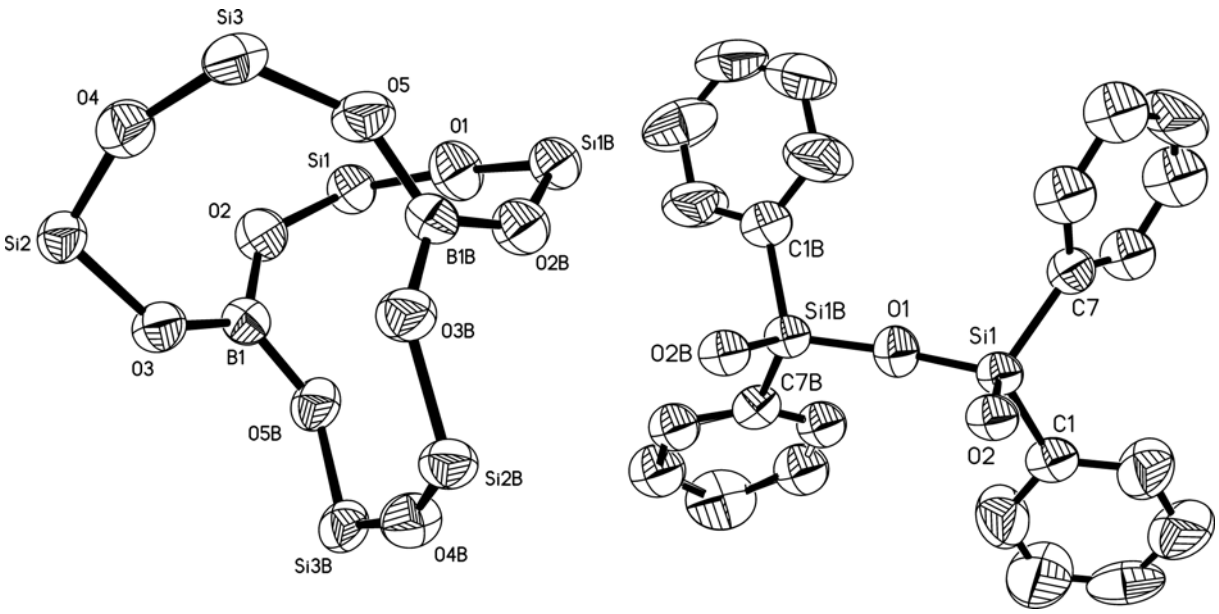


Figure 8.14. Structures of bicyclic boron compound **123**.

Silanes bearing $SiCl_3$ or $Si(R^1)Cl_2$ moieties (**29**, **37 - 40**) react with bis(trimethylstannyl)ethyne to give either allenes or borolenes. The borolenes obtained are new compounds. Among the borolene derivatives two examples (**124c** and **126c**) were obtained as crystalline materials (Figure 8.15) and their structures were determined.

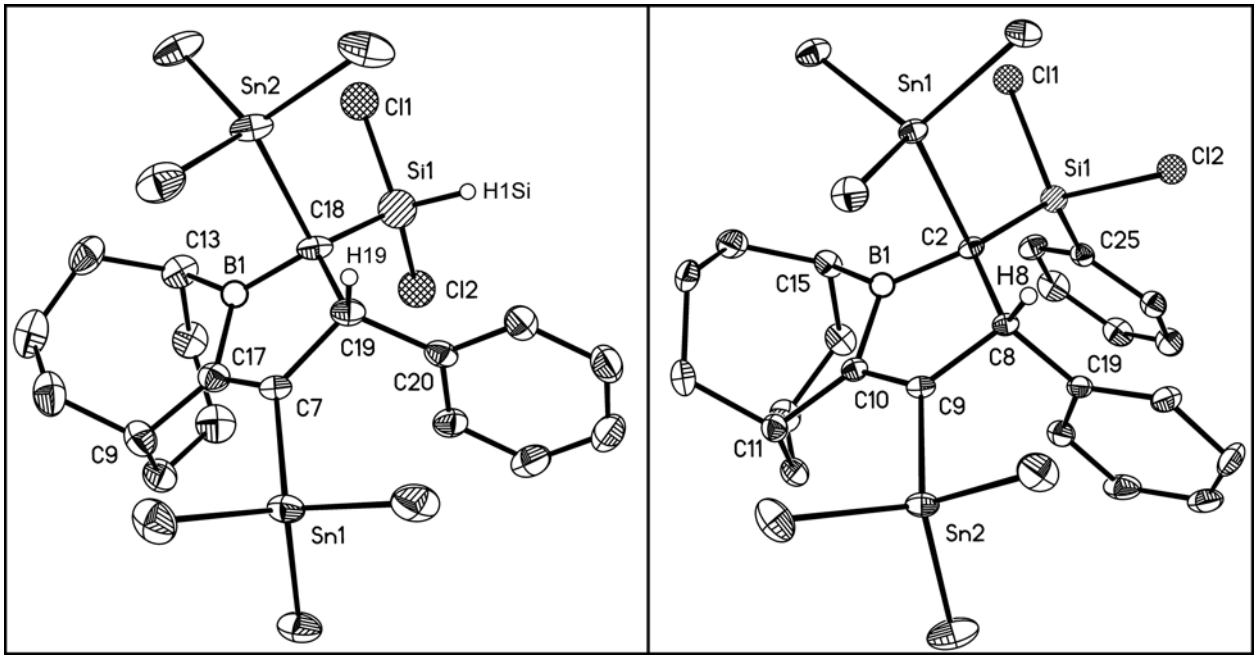
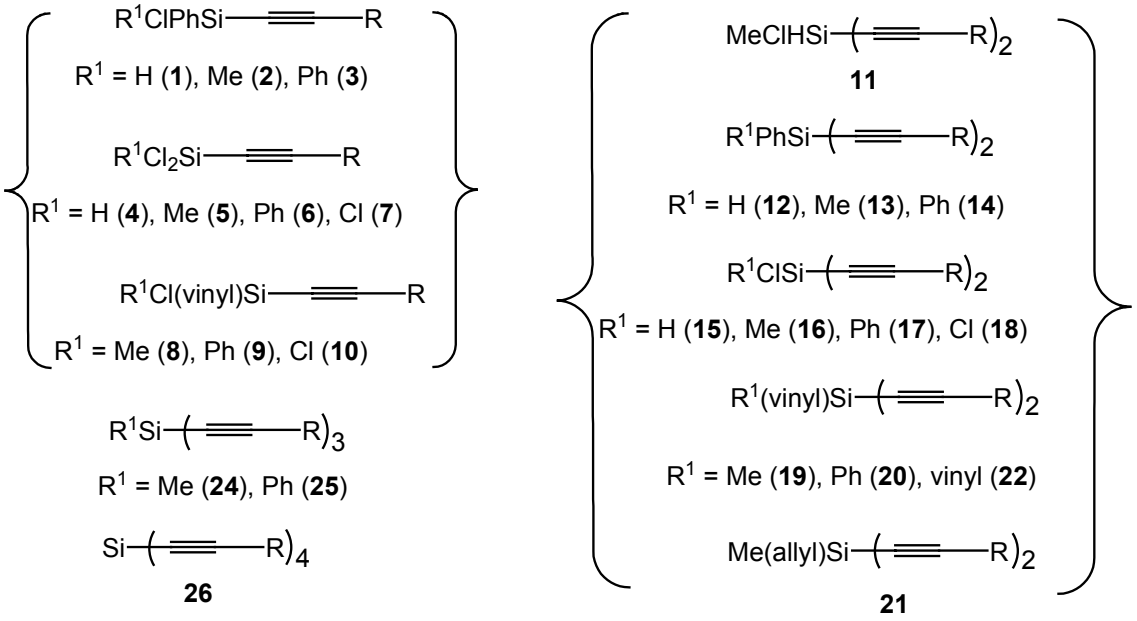


Figure 8.15. Molecular structure of **124c** (left view) and **126c** (right view).

9. ZUSAMMENFASSUNG

Im Verlauf dieser Doktorarbeit wurden neue Alkin-1-ylsilane hergestellt, charakterisiert und ihre Anwendung sowohl in 1,2-Hydroborierungs- und 1,1-Organoborierungsreaktionen als auch in der Kombination dieser Reaktionen wurde gezeigt.

Obwohl man diese Silane (vgl. Schema 9.1) hauptsächlich als Mischungen erhält, können sie durch konventionelle Methoden wie Destillation oder Kristallisation gereinigt werden (vgl. Abb. 9.1 und Abb. 9.2). Mehrere solcher Silane wurden dabei zum ersten Mal mit modernen NMR-spektroskopischen Methoden und teilweise mit Einkristallstrukturanalyse charakterisiert.



Schema 9.1. Die verschiedenen verwendeten Silane.

Die Monoalkin-1-ylchlorosilane wurden mit BEt_3 bei 100 - 120°C über längere Zeit (bis zu 30 Tage) zur Reaktion gebracht und ihre Reaktivität wurde überprüft.
Erstmals wurde das Verhalten von Et_3B als 1,2-Hydroborierungsreagenz in zahlreichen Reaktionen entdeckt. Die Silane, die zwei oder mehr (bis zu vier) Alkin-1-ylgruppen tragen, wurden für Synthesen unterschiedlicher heterocyclischer Systeme, so z.B. 1-Silacyclobutene, 1-Silacyclopent-2-ene, Siloles und Borolene verwendet. Intermediate wurden, soweit möglich, mit Hilfe von Multikern-NMR-Spektroskopie untersucht (^1H, ^{11}B, ^{13}C, ^{29}Si und ^{119}Sn). Zahlreiche Molekülstrukturen konnten mittels Röntgenstrukturanalyse bestimmt werden.

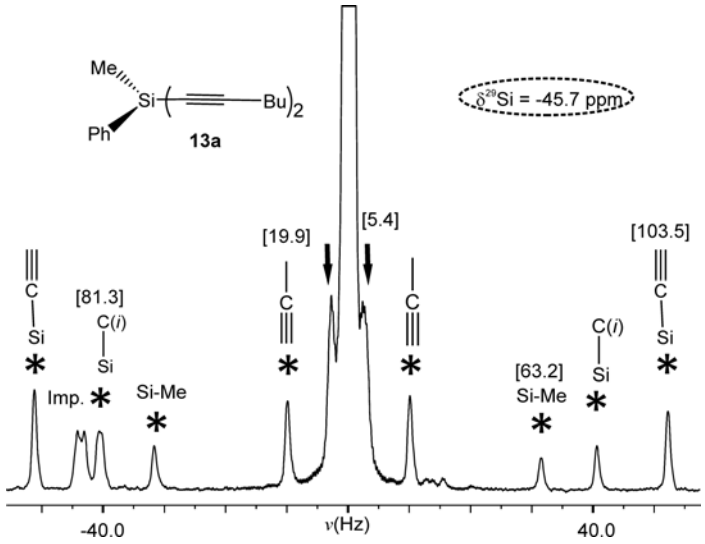


Abb. 9.1. 59.6 MHz $^{29}Si\{^{1}H\}$-NMR-Spektrum des Silans **13a**.

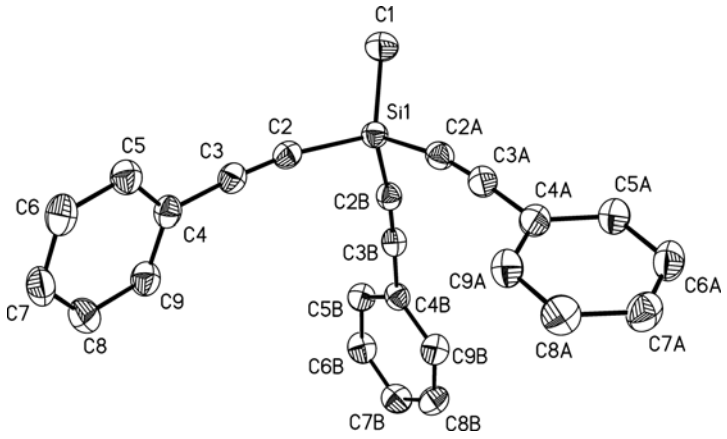


Abb. 9.2. Molekülstruktur von Methyl(triphenylethynyl)silan **24c.**

Die Silane **1 - 26** ergeben bemerkenswert unterschiedliche Produkte bei 1,2-Hydroborierungs- und 1,1-Organoborierungsreaktionen. Die Reaktionen zwischen den Monoalkin-1-ylsilanen **1 - 7** und Et_3B bzw 9-BBN führen selektiv zu den entsprechenden Alkenen (vgl. Abb. 9.3 und Abb. 9.4). Erstmals wurde beobachtet, dass Et_3B auch als 1,2-Hydroborierungsreagenz wirken kann, wenn es mit Alkin-1-yl-trichlorosilanen oder Alkin-1-yldichlorosilanen (**4 - 7**) zur Reaktion gebracht wird. Die thermische 1,2-Dehydroborierung von Et_3B konnte bisher nie beobachtet werden. Dennoch findet diese Reaktion zwischen Et_3B und entsprechenden Silanen statt, und es wird ein Mechanismus mit β-Wasserstoff-Transfer angenommen. Die Produkte der Hydroborierungsreaktionen wurden durch vollständige NMR-Datensätze einerseits und einigen Kristallstrukturen andererseits bestätigt (vgl. Abb. 9.4, **37c**, ein Beispiel, bei dem zum Vergleich 9-BBN verwendet wurde).

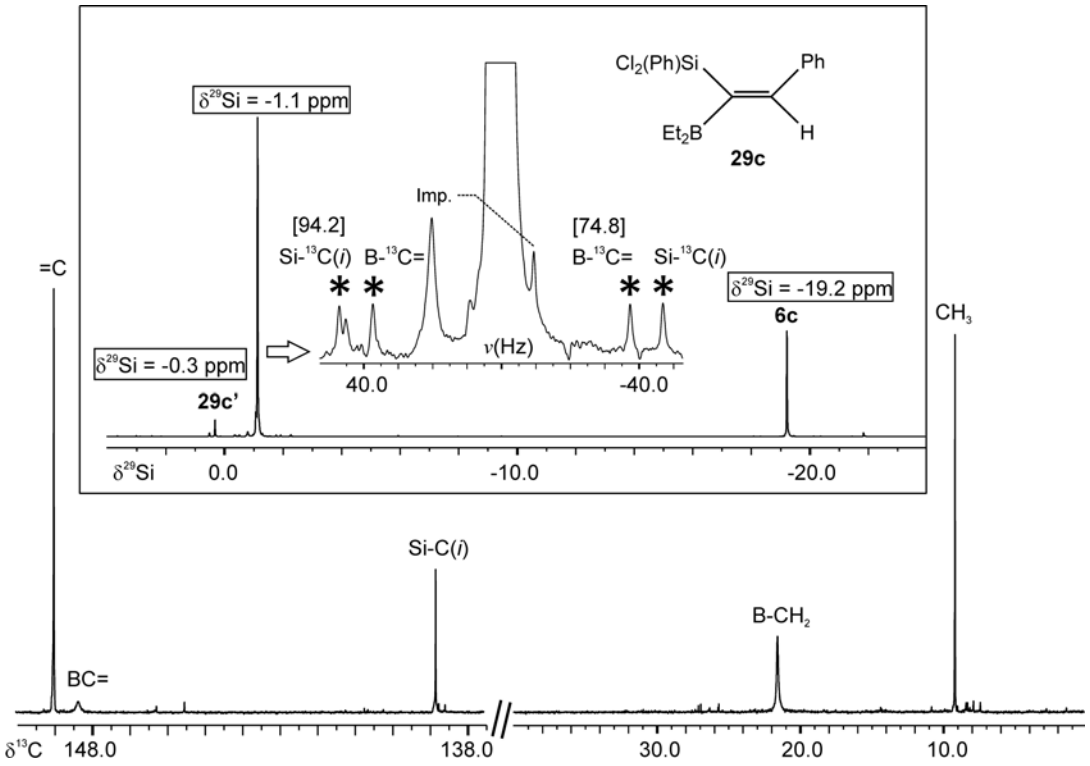


Abb. 9.3. 100.5 MHz $^{13}C\{^1H\}$-NMR-Spektrum von **29c** und $^{29}Si\{^1H\}$-NMR-Spektrum (refokusierte INEPT-Pulsfolge) der Reaktionsmischung mit dem Alken **29c**, dem Edukt Dichloro(phenyl)(phenylethinyl)silan **6c** mit geringen Mengen des (*E*)-Isomeren **29c´**.

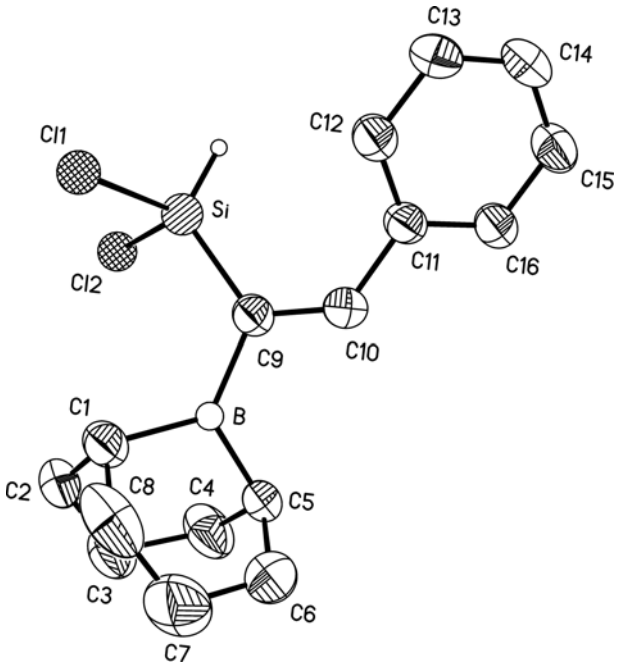
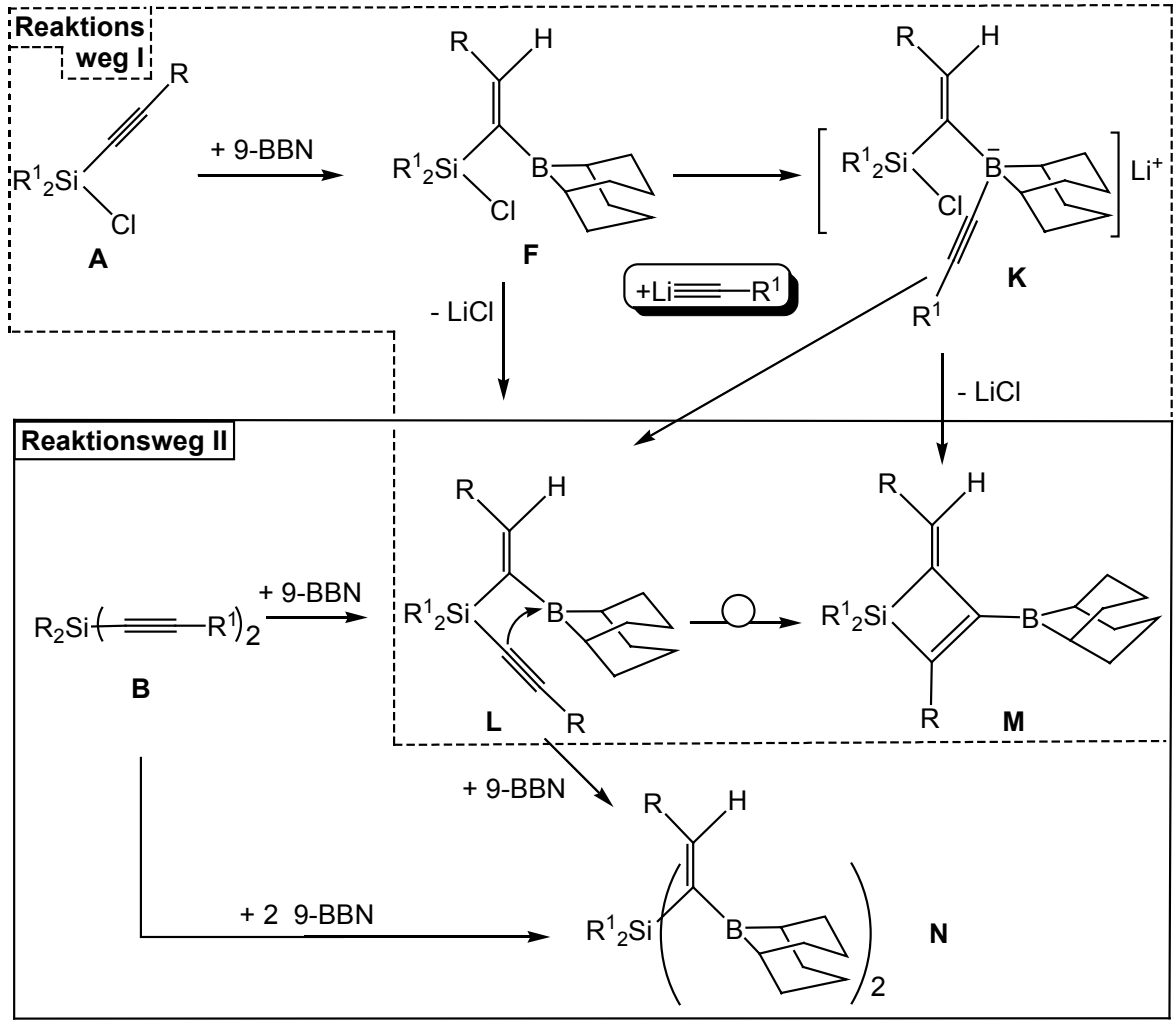


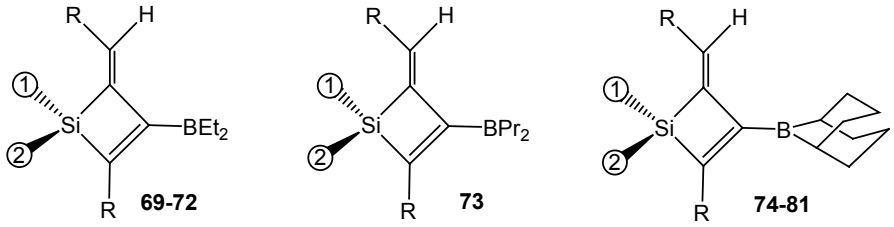
Abb. 9.4. Molekülstruktur des Alkenylsilans **37c**.

Diese Alkene sind attraktive Precursoren für weitere Reaktionen, da das Silicium-Atom noch eine oder mehr reaktive Funktionen trägt (Si-Cl). Sie konnten zum Beispiel in 1-Silacyclobuten-Derivate überführt werden. Die Reaktion läuft über ein Alkyn-1-ylsilane (**L**) oder ein Zwitterionisches Intermediat (**K**) ab. Diese Borat-Intermediate lagern bei RT langsam in Alkin-1-ylsilane (**L**) und reagieren danach bei erhöhten Temperaturen von 80 - 100 °C zu den 1-Silacyclobutenen (**M**). Eine alternative Methode kann verwendet werden um die erwarteten 1-Silacyclobutene zu erhalten. Die Dialkin-1-ylsilane **11 - 18** wurden mit 9-BBN bei 80 - 100 °C erhitzt, dabei bildet sich zuerst die Alkenyl-alkin1-yl-silane als **L**, gefolgt von einer intramolekularen 1,1-Vinylborierung bei der selben Temperatur, was ebenfalls zu **M** führt. Die Molekülstruktur von einem Beispiel (**80a**, Abb. 9.5) konnte mit Hilfe von Röntgenkristallographie zum ersten Mal charakterisiert werden.



Schema 9.2. Synthesen der 1-Silacyclobuten-Derivative über zwei verschiedene Routen, mit Reaktionsmechanismus.

Triorganoborane, wie Et_3B oder Pr_3B, ergeben 1-Silacyclobutene (vgl. Schema 8.3), wenn sie mit entsprechenden Dialkin-1-yl-silanen, die Si-Cl- oder $SiCl_2$-Gruppen tragen, zur Reaktion gebracht werden. Dies ist das Ergebnis einer seltenen Kombination von 1,2-Hydroborierung und 1,1-Organoborierung, ohne den Einsatz einer Bor-Wasserstof-Verbindung.



Schema 9.3. Allgemeine Strukturformeln für die in dieser Arbeit synthetisierten 1-Silacyclobuten-Derivate.

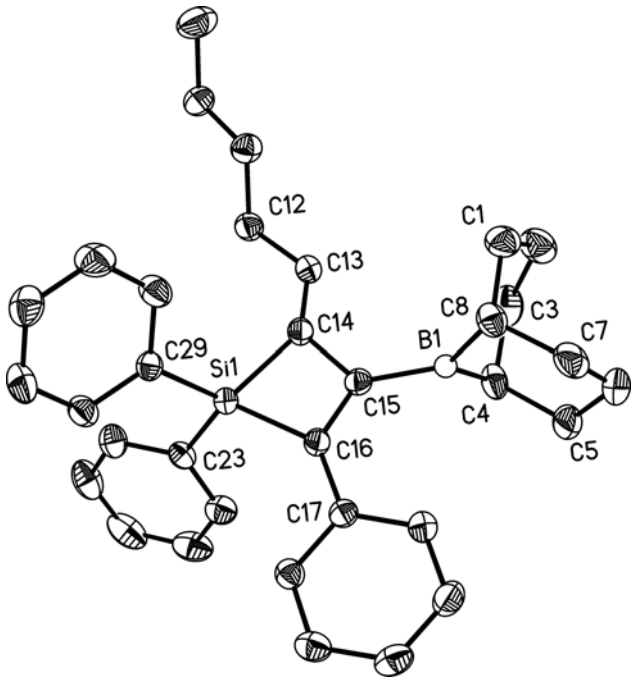
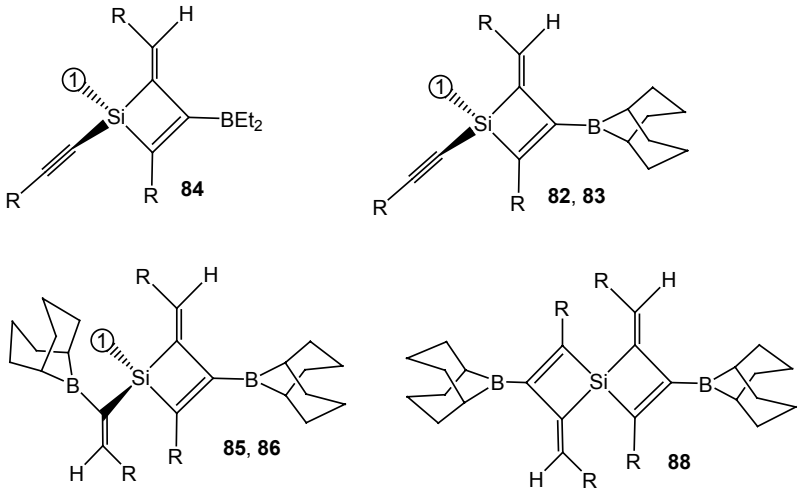


Abb. 9.5. Molekülstruktur des 1-Silacyclobutens **80a.**

Die Silane **24** und **25** reagieren mit einem oder zwei Äquivalenten 9-BBN bei 80 - 100 °C und ergeben die 1-Silacyclobuten-Derivate **82 - 86**. Die Reaktion der Silane **26** mit zwei Äquivalenten 9-BBN ergibt die Spirosilan **88**. Das erste Beispiel für solche Spirosilane (**88d**) wurde mit Hilfe der Röntgenstrukturanalyse charakterisiert (vgl. Abb. 9.6).



Schema 9.4. 1-Silacyclobuten-Derivate, die Spirosilane beinhalten. Die Gruppe (1) am Silicium-Atom ist für jedes betreffende Derivat erwähnt.

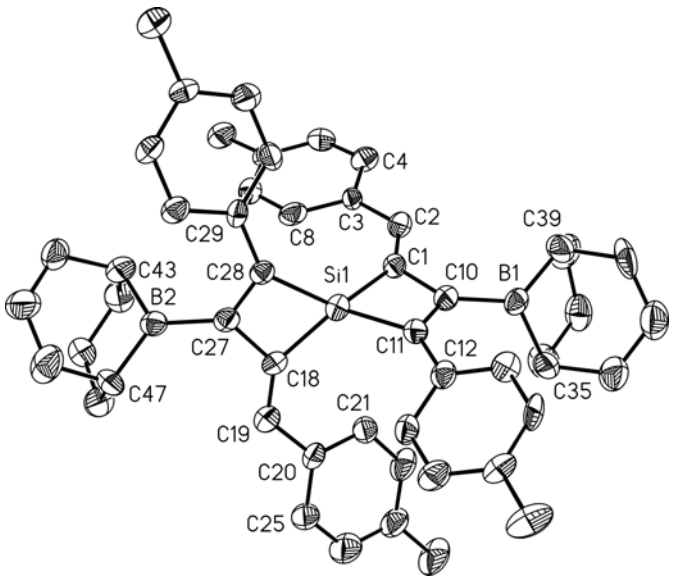


Abb. 9.6. Molekülstruktur des Silans **88d**.

Die Reaktion zwischen Alkin-1-yl-vinylsilanen **8 - 10**, **19**, **20** und **21** mit 9-BBN zeigt, dass 9-BBN bevorzugt die $CH=CH_2$- anstatt der C≡C-Einheit mittels 1,2-Hydroborierung angreift und durch 1,1-Organoborierung ein nachfolgender Ringschluss zu den 1-Silacyclopent-2-en-Derivaten **89 - 95** und den 1-Silacyclohex-2-enen **96** und **97** führt. Zum ersten Mal konnte die Molekülstruktur eines 1-Silacyclopent-2-ens, das eine Si-Cl-Gruppe trägt, mittels Röntgenstrukturanalyse bestimmt werden (vgl. Abb. 9.7).

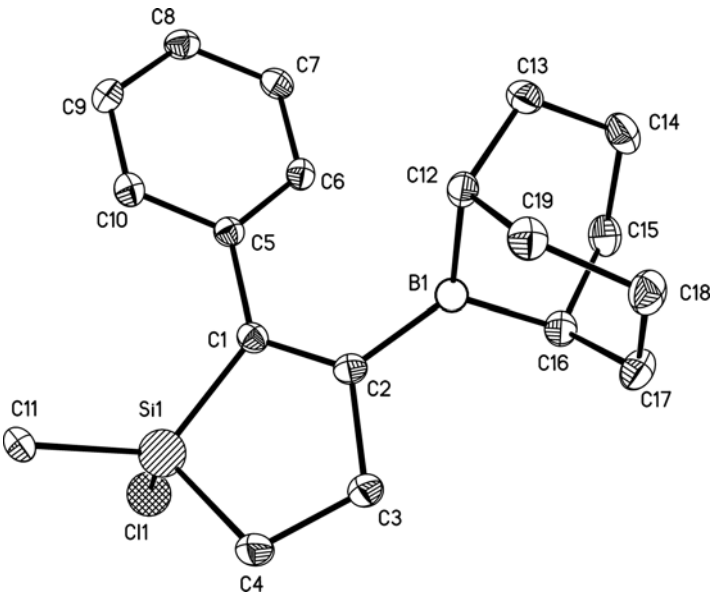


Abb. 9.7. Molekülstruktur von 2-(9-Borabicyclo[3.3.1]nonyl)-1-chloro-1-methyl-2-phenyl-1-silacyclopent-2-en **89c**.

Dialkin-1-yl(divinyl)silane ergeben mit zwei Äquivalenten 9-BBN Spirosilane. Die Bildung dieser Spirosilane wurde in Lösung untersucht und eine Molekülstruktur für **89c** wurde mit Hilfe der Röntgenstrukturanalyse erhalten (vgl. Abb. 9.8).

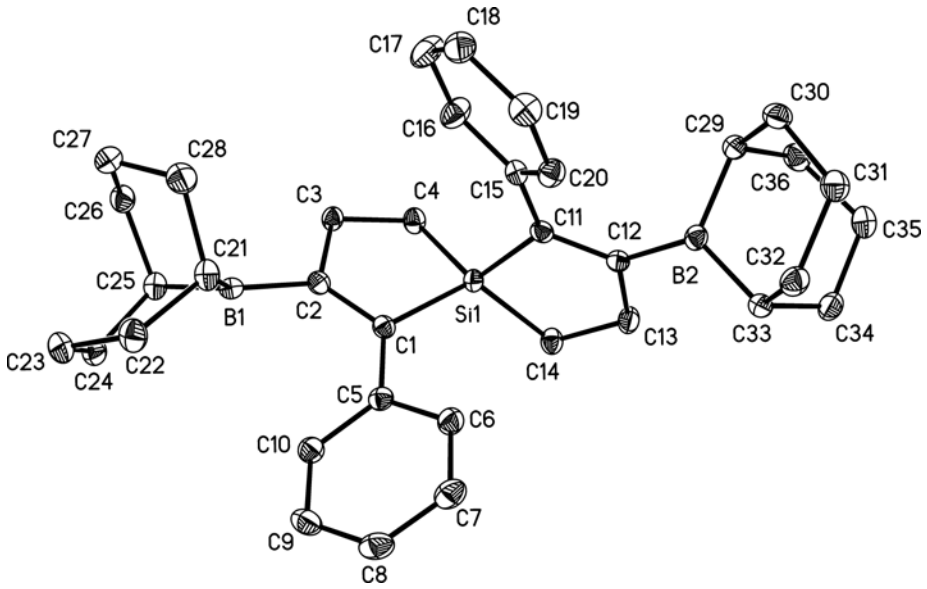


Abb. 9.8. Molekülstruktur von 2,7-bis[9-(9-borabicyclo[3.3.1]nonyl)]-1,6-diphenyl-5-silaspiro[4.4]nona-1,6-dien **100c**.

Die Silacyclopent-2-en- und Silacyclohex-2-en-Derivative mit Spirostruktur wurden für Protodeborylierungsreaktionen verwendet. Sie reagieren bei 23 °C mit Essigsäure in unpolaren Lösungsmitteln (Pentan, Hexan oder Toluol) und ergeben

die entsprechenden protodeborylierten Produkte. Die Bor-Sauerstoff-Verbindung **142** wurde in Lösung untersucht, isoliert und mit Hilfe der Röntgenstrukturanalyse charakterisiert (vgl. Abb. 9.9).

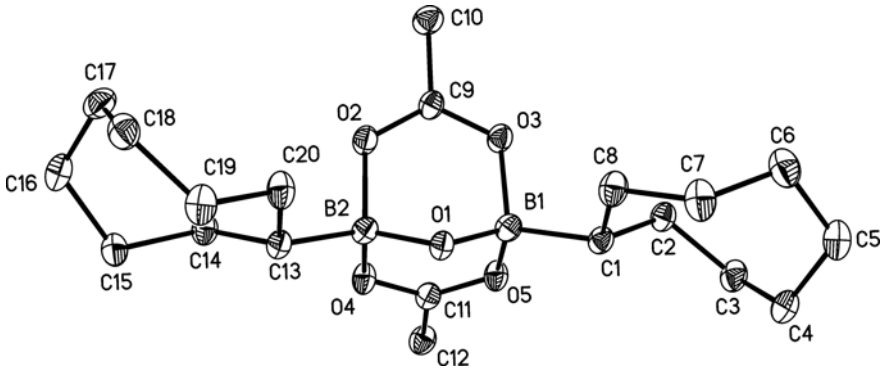


Abb. 9.9. Molekülstruktur der bicyclischen Bor-Sauerstoff-Verbindung **142**.

Alle protodeborylierten Produkte wurden als ölige Flüssigkeiten oder als kristallines Material erhalten. Die Molekülstrukturen des 1-Silacyclopent-2-ens **90c - P** und des Spirosilans **100c - P** wurden mit Hilfe der Röntgenstrukturanalyse ermittelt (vgl. Abb. 9.10 und Abb. 9.11).

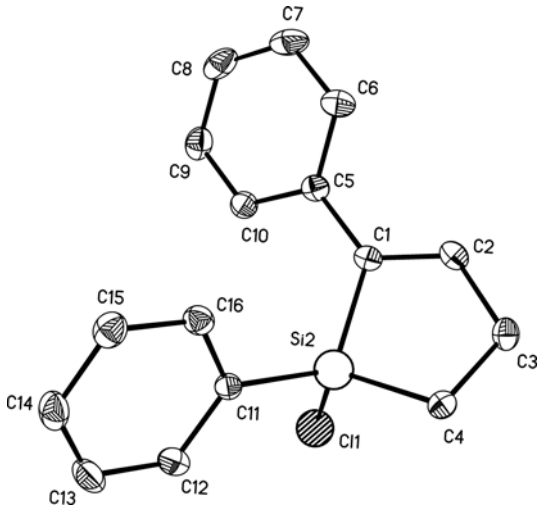


Abb. 9.10. Molekülstruktur von 1-Chloro-1,2-diphenyl-1-silacyclopent-2-en **90c - P**.

Viele Dialkinylsilane reagieren mit BEt_3 unter extremen Bedingungen (bei 100 - 120 °C über einen Zeitraum von mehreren Tagen) um Silole, in Folge einer 1,1-Ethylborarierung gefolgt von einer 1,1-Vinylborarierung, zu ergeben. Dies ist eine sehr brauchbare Methode und man erhält nahezu reine Silole (vgl. Schema 9.5). Ihr synthetisches Potential wurde erforscht. Die Et_2B-Gruppe wurde mit Essigsäure in nahezu allen Fällen bei Raumtemperatur entfernt. Es konnte beobachtet werden,

dass die Si-H-Funktion keine Essigsäure toleriert, wobei eine Si-OAc-Gruppe am entsprechenden Silolring eingeführt wird (vgl. Schema 9.5).

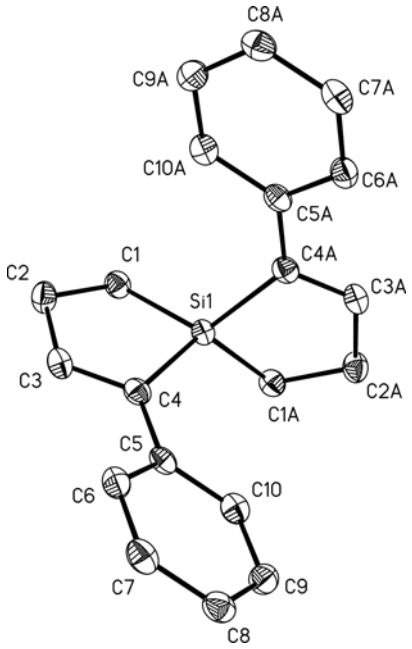
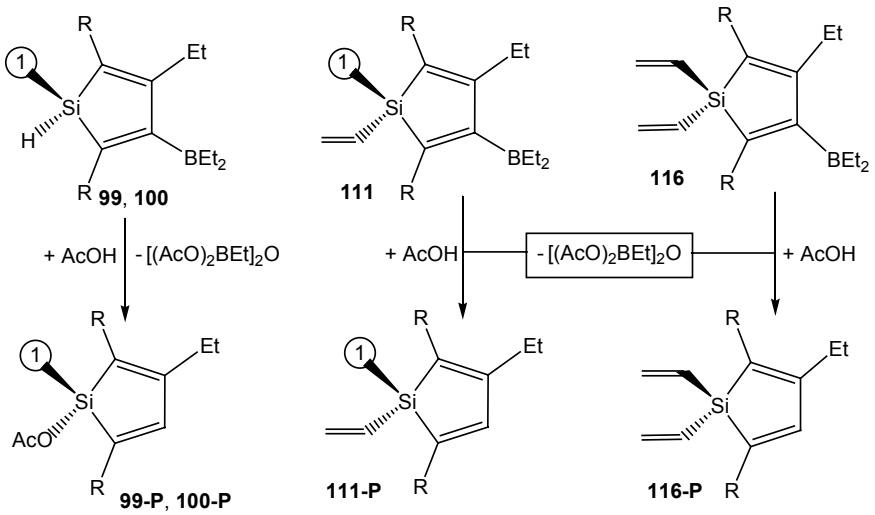


Abb. 9.11. Molekülstruktur von 1,6-Diphenyl-1-silaspiro[4.4]nona-1,6-dien **100c - P**.



Schema 9.5. Charakteristische Beispiele für Silole.

Die Reaktion zwischen **12c** und 9-Ethyl-9-borabicyclo[3.3.1]nonan ergibt das Silol **109c** als kristallines Material, das für die Röntgenstrukturanalyse geeignet ist. Dies ist das erste Beispiel für eine Kristallstruktur eines Silols, das mit Hilfe der 1,1-Organoborarierung erhalten wurde (vgl. Abb. 9.12).

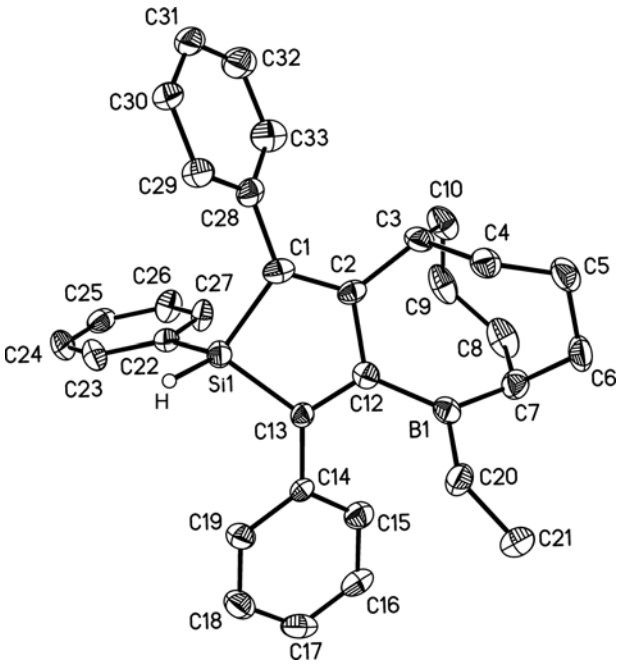


Abb. 9.12. Molekülstruktur von Silol **109c**

Bei der Untersuchung der Reaktivität der Si-Cl-Funktion und dem Verhalten der Alkenylsilane **35c** und **36c** an Luft konnte kristallines Material erhalten werden, das mit Hilfe der Röntgenstrukturanalyse die Molekülstrukturen der neuen Heterocyclen **121** und **123** (vgl. Abb. 9.13 und Abb. 9.14) und von 9-Hydroxy-9-borabicyclo[3.3.1]nonan **122** ergab

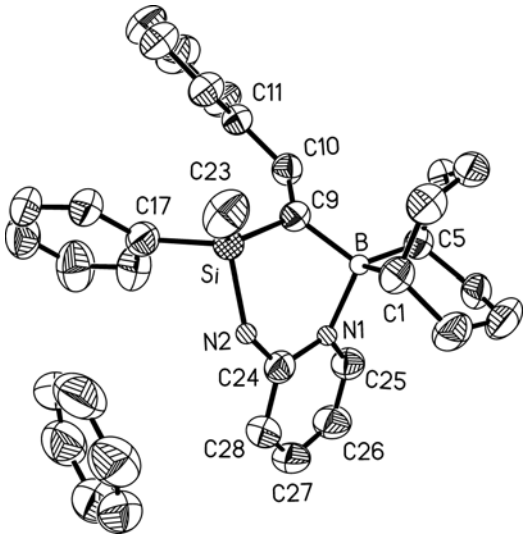


Abb. 9.13. Molekülstruktur des Heteropolycyclus **121**.

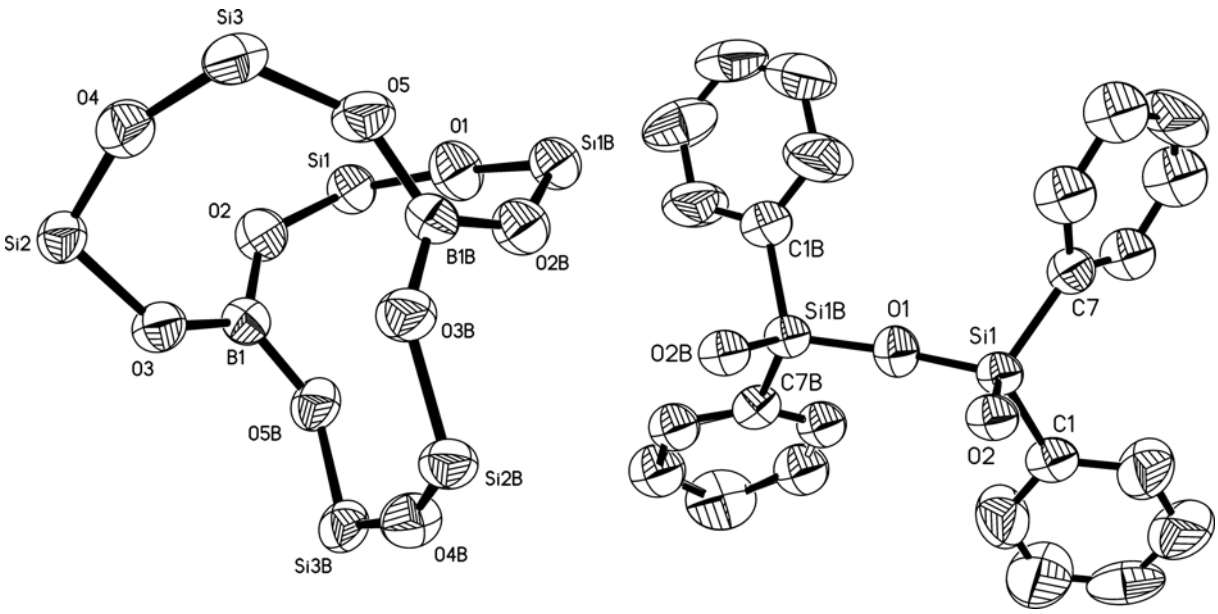


Abb. 9.14. Molekülstruktur der bicyclischen Bor-Verbindung **123**.

Silane, die einen $SiCl_3$- oder $Si(R^1)Cl_2$-Rest tragen (**29**, **37 - 40**), reagieren mit Bis(trimethylstannyl)ethin unter der Bildung von Allenen oder Borolenen. Die gewonnenen Borolene stellen neue Verbindungen dar. Von den Borolenen wurden zwei Beispiele (**124c** und **126c**) als einkristallines Material erhalten (vgl. Abb. 9.15).

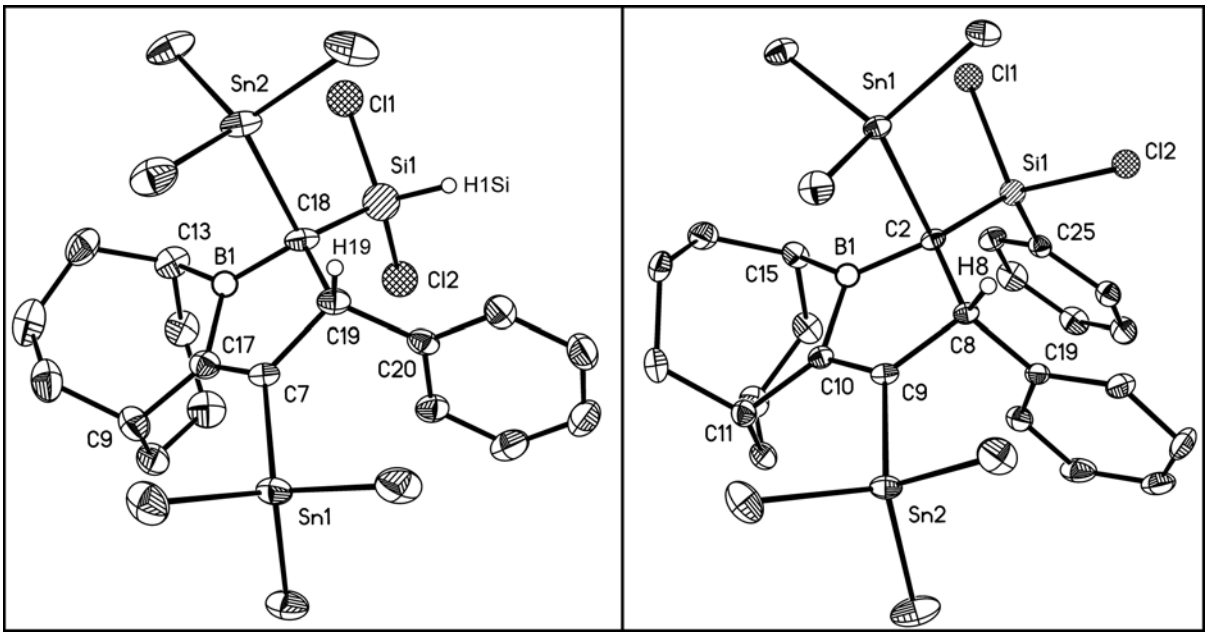


Abb. 9.15. Molekülstruktur von **124c** (linke Seite) und **126c** (rechte Seite).

10. EXPERIMENTAL

10.1. Methods and measurements

All preparative work was carried out under argon (Ar) atmosphere, observing necessary precautions to exclude traces of oxygen and moisture. The experiments were performed throughout in oven-dried Schlenk-type glassware. The solvents (pentane, hexane, toluene diethylether and THF) were dried and distilled prior to use. Deuterated solvents (C_6D_6, $CDCl_3$ and THF-D_8) were obtained from Cambridge Isotope Laboratories and were kept dry with molecular sieves. Lower temperatures for reactions were attained by using ice bath (0 °C), or dry ice (CO_2) in isopropanol (-78 °C).

10.2. Chemicals used

The alkyn-1-ylsilanes used as starting materials were prepared by treating alkynyl lithium with respective chlorosilanes and were purified by fractional distillation. The tripropylborane (BPr_3) was available (gift by R. Köster, Max-Planck-Institut für Kohlenforschung, Mülheim). [165] The other chemicals used in performing this work were commercial products. They were purchased from different companies and were used as received.

Aldrich: Tetrachlorosilane, trichloro(vinyl)silane, dichloro(methyl)(vinyl)silane, dichloro(methyl)silane, trichloro(phenyl)silane, trichloro(vinyl)silane, 1-hexyne, ethynylbenzene, BuLi in hexane (1.6 M) and 9-BBN.

ACROS: dichloro(methyl)(phenyl)silane, trichloro(methyl)silane.

Fluka: dichloro(phenyl)silane.

Alfa Aesar: 3,3-dimethyl-1-butyne.

ABCR: *p*-Tolylacetylene, 4-(*tert*-butyl)phenylacetylene, dichloro(phenyl)(vinyl)silane, dichloro(divinyl)silane.

Merk: Glacial acetic acid.

Witco Polymer Chemicals + Synthetic Resins: Triethylborane (BEt_3).

10.3. Instrumentation

10.3.1. NMR spectroscopy

All the NMR measurements (^{11}B, ^{13}C, ^{1}H, ^{29}Si and ^{119}Sn) were carried out as C_6D_6, $CDCl_3$ or THF-D_8 solutions at 23 °C using the following spectrometers,

- Varian Inova 400 MHz and 300 MHz (^{1}H)
- Bruker DRX 500 MHz (^{1}H)
- Bruker ARX 250 MHz (^{1}H)

The spectrometers used for NMR measurements were equipped with multinuclear units. The sample solutions were prepared using deutrated solvents (*ca.* 10-15% v/v) in 5 mm tubes. The chemical shifts $\delta^{1}H$ are given to (± 0.03 ppm), $\delta^{13}C$, $\delta^{29}Si$ to (± 0.1 ppm) and $\delta^{11}B$ to (± 0.3 ppm). The coupling constants are given in [± 0.4 Hz]. ^{29}Si NMR spectra were measured by using the refocused INEPT pulse sequence, [117,118] based on $^{1}J(^{1}H_{Si\text{-}H},^{29}Si)$ (ca. 180-280 Hz), $^{3}J(^{1}H_{Si\text{-}Ph,\ Si\text{-}Bu},^{29}Si)$/ $^{2}J(^{1}H_{Si\text{-}Me},^{29}Si)$ (ca. 7 Hz) and $^{3}J(^{1}H_{=CH},^{29}Si)$ (20 - 35 Hz) after optimisation of the refocusing delay according to the number of protons. In the ^{1}H-NMR spectra, the multiplicities are abbreviated as s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. The positive sign of chemical shifts indicates high frequency (down field) shift, whereas the negative sign shows lower frequency (high field) shift with respect to the following reference standards.

^{1}H	$SiMe_4$, ext., Ξ ^{1}H = 100.000000 MHz, $\delta(C_6D_5H)$ = 7.15, $\delta(CHCl_3)$ = 7.24, δ(THF-D_7H) = 1.73
^{11}B	BF_3-Et_2O, ext., Ξ ^{11}B = 32.083971 MHz, δ = 0
^{13}C	$SiMe_4$, ext., Ξ ^{13}C = 25.145004 MHz, $\delta(C_6D_6)$ = 128.0, $\delta(CDCl_3)$ = 77.0, δ(THF-D_8) = 25.4
^{29}Si	$SiMe_4$, ext., Ξ ^{29}Si = 19.867184 MHz, $\delta = 0$
^{119}Sn	$SnMe_4$, ext., Ξ ^{13}C = 37.290665 MHz, δ = 0

10.3.2. Mass spectrometry

The EI-Mass spectra were recorded on Finnigan MAT 8500 spectrometer with direct inlet system using 70 eV energy for ionisation. The samples were injected as solutions in toluene.

10.3.3. X-ray diffraction analysis

Suitable crystals were selected in perfluorinated oil [166] at room temperature and analyses were carried out at low temperature (≈ 190 K) using a STOE IPDS II machine equipped with an Oxford cryostream low-temperature unit. Otherwise some crystals of appropriate size were sealed under argon in Lindemann capillaries and the data collections were carried out at ambient temperature using a STOE IPDS I difractometer. Structure solutions and refinements were accomplished using SIR97, [167] SHELXL-97 [168] and WinGX [169] or SHELXTL V 5.1 programmes.

10.3.4. Melting point measurements

The melting points (uncorrected) were determined using a Büchi 510 melting point apparatus.

10.4. Syntheses

10.4.1. Syntheses of alkyn-1-ylsilanes

10.4.1.1. *Syntheses of monoalkyn-1-yl(chloro)silanes **1 - 7***

General procedure: A suspension of Li-C≡C-R (50 mmol; R = Bu, ^{t}Bu, Ph, 4-Me-C_6H_4) in hexane was freshly prepared at 0 °C and the solution was cooled to –78 °C. Then the respective chlorosilanes (in four- to eightfold excess) were added slowly with constant stirring. The reaction mixtures were slowly warmed to room temperature and kept stirring for 3 - 4 h. Insoluble materials were filtered off and all volatiles were removed in *vacuo*. The colorless oily residues left were analyzed by NMR spectroscopy and were identified as the mixtures of desired products, together with other silanes, where more than one chlorine atoms were replaced by alkynyl functions. Pure sample of alkyn-1-ylsilanes were obtained by fractional distillation. The overall yield achieved was 60 - 70 % for silanes **1** - **3**, 30 - 35 % for silanes **4** - **6** and 20 - 25 % for silanes **7**.

1a: B. p. = 105 - 115 °C/0.375 Torr; ^{1}H NMR (300 MHz): δ = 2.2, 1.5, 1.4, 0.9 (m, m, m, t, 9H, Bu), 4.8 (s, 1H, $^{1}J(^{1}H,^{29}Si)$ = 203.9 Hz, Si-H), 7.3 - 7.7 (m, 5H, Si-Ph).

1c: B. p. = 115 - 126 °C/0.375 Torr; ^{1}H NMR (300 MHz): δ = 5.4 (s, 1H, $^{1}J(^{1}H,^{29}Si)$ = 214.3 Hz, Si-H), 7.1 - 7.7 (m, 10H, Si-Ph, Ph).

2a: B. p. = 82 - 88 °C/0.375 Torr; ^{1}H NMR (300 MHz): δ = 0.6 (s, 3H, Si-Me), 2.2, 1.4, 1.3, 0.7 (m, m, m, t, 9H, Bu), 7.2 - 7.6 (m, 5H, Si-Ph).

2c: B. p. = 125 - 130 °C/0.375 Torr; ^{1}H NMR (300 MHz): δ = 0.8 (s, 3H, Si-Me), 7.7, 7.5, 7.4, 7.2 (m, m, m, m, 10H, Si-Ph, Ph).

3a: B. p. = 110 - 120 °C/0.375 Torr; ^{1}H NMR (300 MHz): δ = 2.5, 1.5, 1.7, 1.0 (m, m, m, t, 9H, Bu), 7.5 - 7.9 (m, 10H, $SiPh_2$).

3c: B. p.= 170 - 175 °C/0.375 Torr; ^{1}H NMR (300 MHz): δ = 7.4 - 7.9 (m, 15H, $SiPh_2$, Ph).

5a: B. p. = 32 - 34 °C/1.1 Torr; ^{1}H NMR (400 MHz): δ = 0.4 (s, 3H, $^2J(^1H,^{29}Si)$ = 7.8 Hz, Si-Me), 1.9, 1.2, 0.7 (t, m, t, 9H, Bu).

5c: B. p. = 72 - 75 °C/0.3 Torr; ^{1}H NMR (400 MHz): δ = 0.6 (s, 3H, $^2J(^1H,^{29}Si)$ = 8.4 Hz, Si-Me), 6.8, 7.2 (m, m, 5H, Ph).

6a: B. p. = 85 - 86 °C/9x10^{-2} Torr; ^{1}H NMR (300 MHz): δ = 2.3, 1.5, 1.4, 0.5 (t, m, m, t, 9H, Bu), 7.4, 7.8 (m, m, 5H, Si-Ph).

6b: B. p. = 74 - 76 °C/1.5x10^{-2} Torr; ^{1}H NMR (400 MHz): δ = 0.9 (s, 9H, ^{t}Bu), 7.7, 7.1 (m, m, 5H, Si-Ph).

6c: B. p. = 120 - 125 °C/0.105 Torr; ^{1}H NMR (300 MHz): δ = 7.2 - 7.5, 7.9 (m, m, 15H, Ph, $SiPh_2$).

7a: B. p. = 30 °C/0.3 Torr; ^{1}H NMR (300 MHz): δ = 1.9, 1.2, 0.7 (t, m, t, 9H, Bu).

7c: B. p. 70 - 75 °C/0.3 Torr; ^{1}H NMR (300 MHz): δ = 6.8 - 7.1 (m, 5H, Ph).

10.4.1.2. *Syntheses of the monoalkyn-1-yl(vinyl)silanes,* ***8 - 10***

A suspension of Li-C≡C-Bu (50 mmol) at 0 °C, was prepared in hexane (60 mL) and the solution was cooled to -78 °C. Then dichloro(methyl)(vinyl)silane (21.0 mL, in threefold excess) was added slowly with constant stirring. The reaction mixture was warmed to room temperature and kept stirring for 5 h. The solution was filtered off and all the volatile materials were removed in a vacuum. The colorless oily residue was identified as a mixture of $MeClSi(H_2C{=}CH)(C{\equiv}C\text{-}Bu)$, **8a** and $Me(H_2C{=}CH)Si(\text{-}C{\equiv}C\text{-}R)_2$, **19a** (*vide infra*), as a side product. Pure sample of **8a** was obtained by fractional distillation. The same work up procedure was repeated for the syntheses of silanes **9** and **10**.

8a: B. p. = 38 - 39 °C/0.1 Torr; ^{1}H NMR (400 MHz): δ = 0.5 (s, 3H, $^2J(^1H,^{29}Si)$ = 7.5 Hz, Si-Me), 1.9, 1.2, 0.7 (t, m, t, 9H, Bu), 5.8 (dd, 1H, $^2J(^1H,^1H)$ = 4.1 Hz, $^3J(^1H,^1H)$ =

13.5 Hz, H_2C=), 5.9 (dd, 1H, $^2J(^1H,^1H)$ = 4.1 Hz, $^3J(^1H,^1H)$ = 20.2 Hz, H_2C=), 6.1 (dd, 1H, $^3J(^1H,^1H)_{cis}$ = 13.5 Hz, $^3J(^1H,^1H)_{trans}$ = 20.2 Hz, Si-HC=).

8b: B. p. = 39 - 41 °C/1.1×10^{-2} Torr; ^{1}H NMR (400 MHz): δ = 0.4 (s, 3H, $^2J(^1H,^{29}Si)$ = 7.4 Hz, Si-Me), 1.1 (s, 9H, ^{t}Bu), 5.4 (dd, 1H, $^2J(^1H,^1H)$ = 4.3 Hz, $^3J(^1H,^1H)$ = 13.4 Hz, =CH_2), 5.5 (dd, 1H, $^2J(^1H,^1H)$ = 4.1 Hz, $^3J(^1H,^1H)$ = 20.0 Hz, =CH_2), 5.6 (dd, 1H, $^3J(^1H,^1H)_{cis}$ = 13.5 Hz, $^3J(^1H,^1H)_{trans}$ = 20.1 Hz, Si-CH=).

8c: B. p. = 55 - 58 °C/9×10^{-2} Torr; ^{1}H NMR (400 MHz): δ = 0.5 (s, 3H, $^2J(^1H,^{29}Si)$ = 7.6 Hz, Si-Me), 5.9 (dd, 1H, $^2J(^1H,^1H)$ = 3.9 Hz, $^3J(^1H,^1H)$ = 13.4 Hz, =CH_2), 6.0 (dd, 1H, $^2J(^1H,^1H)$ = 4.1 Hz, $^3J(^1H,^1H)$ = 20.3 Hz, =CH_2), 6.1 (dd, 1H, $^3J(^1H,^1H)_{cis}$ = 13.4 Hz, $^3J(^1H,^1H)_{trans}$ = 20.3 Hz, Si-HC=), 6.9, 7.3 (m, m, 5H, Ph).

9a: B. p. = 115 - 120 °C/1.8×10^{-2} Torr; ^{1}H NMR (400 MHz): δ = 1.9, 1.2, 0.6 (t, m, t, 9H, Bu), 5.9 (dd, 1H, $^2J(^1H,^1H)$ = 4.0 Hz, $^3J(^1H,^1H)$ = 13.7 Hz, =CH_2), 6.0 (dd, 1H, $^2J(^1H,^1H)$ = 4.0 Hz, $^3J(^1H,^1H)$ = 19.9 Hz, =CH_2), 6.2 (dd, 1H, $^3J(^1H,^1H)_{cis}$ = 13.4 Hz, $^3J(^1H,^1H)_{trans}$ = 19.9 Hz, Si-HC=), 7.7, 7.1 (m, m, 5H, Si-Ph).

9c: B. p. = 122 - 125 °C/2.1×10^{-2} Torr; ^{1}H NMR (400 MHz): δ = 6.0 (dd, 1H, $^2J(^1H,^1H)$ = 4.0 Hz, $^3J(^1H,^1H)$ = 13.5 Hz, =CH_2), 6.2 (dd, 1H, $^2J(^1H,^1H)$ = 4.1 Hz, $^3J(^1H,^1H)$ = 20.1 Hz, =CH_2), 6.3 (dd, 1H, $^3J(^1H,^1H)_{cis}$ = 13.4 Hz, $^3J(^1H,^1H)_{trans}$ = 20.1 Hz, Si-HC=), 6.9, 7.2, 7.3, 7.8 (m, m, m, m, 10H, Si-Ph, Ph).

10a: B. p. = 38 - 42 °C/0.3 Torr; ^{1}H NMR (400 MHz): δ = 1.8, 1.1, 0.7 (t, m, t, 9H, Bu), 5.8 (dd, 1H, $^2J(^1H,^1H)$ = 3.6 Hz, $^3J(^1H,^1H)$ = 13.4 Hz, =CH_2), 6.0 (dd, 1H, $^3J(^1H,^1H)_{cis}$ = 13.4 Hz, $^3J(^1H,^1H)_{trans}$ = 19.8 Hz, Si-HC=), 6.1 (dd, 1H, $^2J(^1H,^1H)$ = 3.7 Hz, $^3J(^1H,^1H)$ = 19.9 Hz, =CH_2); MS: *m/z* (%) = 207 (17) [M^+], 192 (5) [M^+-CH_3], 180 (10) [M^+-C_2H_3], 171 (25) [M^+-Cl], 81 (73) [$C_6H_9^+$], 43 (98) [$C_3H_7^+$], 41 (100).

10c: B. p. = 54 - 55 °C/0.075 Torr; ^{1}H NMR (400 MHz): δ = 5.8 (dd, 1H, $^2J(^1H,^1H)$ = 3.5 Hz, $^3J(^1H,^1H)$ = 13.5 Hz, =CH_2), 6.0 (dd, 1H, $^2J(^1H,^1H)_{cis}$ = 13.5 Hz, $^3J(^1H,^1H)_{trans}$ = 19.8 Hz, Si-HC), 6.1 (dd, 1H, $^2J(^1H,^1H)$ = 3.5 Hz, $^3J(^1H,^1H)$ = 19.4 Hz, =CH_2), 6.8, 7.1 (m, m, 5H, Ph).

10.4.1.3. *Syntheses of dialkyn-1-ylsilanes **11 - 18***

Dialkyn-1-ylsilanes **11 - 18** were side products accompanying the silanes **1** - **7**. They were obtained as a result of two Si-Cl functions substituted by alkynyl groups and were collected as second fractions during fractional distillation. The presence of a little amount of monoalkyn-1-ylsilanes required further purification by a second distillation. After getting pure samples, they were studied by multinuclear NMR

spectroscopy and were used in further reactions. Derivatives of the silane **11** were prepared at 0 °C by the reaction of two equivalents (20 mmol) of alkynyl lithium with one equivalent (10 mmol, 1.7 mL) of dichloro(methyl)silane. The reaction mixture was warmed to room temperature and was heated to 40 °C for 3 - 4 h. The solid was separated and all volatiles were removed under reduced pressure. The required silanes were obtained as oily liquids (**11a**) or solid materials (**11c**, **11d**) (overall yield ca. 95%).

11a: ^{1}H NMR (400 MHz): δ = 0.3 (d, 3H, $^{3}J(^{1}H,^{1}H)$ = 3.8 Hz, Si-Me), 2.0, 1.2, 0.7 (t, m, t, 18H, Bu), 4.5 (m, 1H, $^{1}J(^{1}H,^{29}Si)$ = 216.4 Hz, Si-H).

11c: ^{1}H NMR (400 MHz): δ = 0.4 (d, 3H, $^{3}J(^{1}H,^{1}H)$ = 3.9 Hz, $^{3}J(^{1}H,^{29}Si)$ = 8.0 Hz, Si-Me), 4.8 (q, 1H, $^{1}J(^{1}H,^{29}Si)$ = 223.7 Hz, Si-H), 7.3, 6.9 (m, m, 10H, Ph).

11d: ^{1}H NMR (400 MHz): δ = 0.4 (d, 3H, $^{3}J(^{1}H,^{1}H)$ = 3.9 Hz, Si-Me), 5.0 (q, 1H, $^{1}J(^{1}H,^{29}Si)$ = 221.8 Hz, Si-H), 7.3, 6.7, 1.9 (m, m, s, 14H, 4-Me-C_6H_4).

12a: ^{1}H NMR (300 MHz): δ = 2.2, 1.5, 1.4, 0.9 (t, m, m, t, 18H, Bu), 4.8 (s, 1H, $^{1}J(^{1}H,^{29}Si)$ = 224.8 Hz, Si-H), 7.7, 7.3 (m, m, 5H, Si-Ph).

12c: ^{1}H NMR (300 MHz): δ = 5.5 (s, 1H, $^{1}J(^{1}H,^{29}Si)$ = 228.5 Hz, Si-H), 7.9, 7.3, 7.2, 6.9 (m, m, m, m, 15H, $^{3}J(^{1}H,^{29}Si)$ = 7.0 Hz, Si-Ph, Ph).

13a: ^{1}H NMR (400 MHz): δ = 0.5 (s, 3H, Si-Me), 1.9, 1.2, 0.7 (t, m, t, 18H, Bu), 7.8, 7.2 (m, m, 5H, Si-Ph).

13c: ^{1}H NMR (400 MHz): δ = 0.5 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 7.1 Hz, Si-Me), 7.7, 7.1, 7.0, 6.6 (m, m, m, m, 15H, Si-Ph, Ph).

14a: ^{1}H NMR (400 MHz): δ = 2.0, 1.2, 0.6 (t, m, t, 18H, Bu), 8.0, 7.1 (m, m, 10H, $SiPh_2$).

15c: ^{1}H NMR data already reported. [77]

16a: B. p. = 83 - 85 °C/2.1×10^{-2} Torr; ^{1}H NMR (400 MHz): δ = 0.6 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 8.2 Hz, Si-Me), 1.7, 1.1, 0.5 (t, m, t, 18H, Bu).

16c: B. p. = 145 - 150 °C/6.8×10^{-2} Torr; ^{1}H NMR (400 MHz): δ = 0.5 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 8.0 Hz, Si-Me), 7.1, 6.6 (m, m, 10H, Ph).

17c: B. p. = 192 - 196 °C/0.105 Torr; ^{1}H NMR (400 MHz): δ = 8.0, 7.2, 6.8 (m, m, m, 15H, Si-Ph, Ph).

18a: B. p. = 83 °C/1×10^{-3} Torr; ^{1}H NMR (400 MHz): δ = 1.8, 1.1, 0.6 (t, m, t, 18H, Bu).

10.4.1.4. *Syntheses of dialkyn-1-yl(vinyl)silanes (**19**, **20**), dialkyn-1-yl(allyl)silanes (**21**)* and *dialkyn-1-yl(divinyl)silanes (**22**, **23**)*

Dialkyn-1-yl(vinyl)silanes such as **19** and **20** were obtained as side products accompanying the silanes **8** and **9**. They were isolated as described for the aforementioned silanes **12** - **18**. A freshly prepared suspension of hexynyl lithium (25 mmol) in hexane (50 mL) was cooled to -78 °C and dichloro(divinyl)silane (12.5 mmol, 2 mL) was added slowly. The reaction mixture was warmed to room temperature and stirring was continued for 4 - 5 h. Insoluble materials were filtered off and all readily volatile materials were removed in a vacuum. The colorless oily residue was identified as the mixture of **22a** and $Si(CH=CH_2)_2(C\equiv C\text{-}Bu)Cl$ as the side product. These compounds could be separated by fractional distillation to give both pure **22a** and the chlorosilane. The latter $Si(CH=CH_2)_2(C\equiv C\text{-}Bu)Cl$ (3.8 g, 19.2 mmol) was added to a freshly prepared suspension of 4-*tert*-butylphenylethynyl lithium (19.2.mmol) in hexane (60 mL), following identical reaction conditions, and the silane **23a** was obtained as oil (> 99 % from ^1H NMR). The same preparative method was adopted for the preparation of dialkyn-1-yl(divinyl)silanes **22b**, **22c** and **21c**.

19a: ^1H NMR (400 MHz): δ = 0.3 (s, $^2J(^1H,^{29}Si)$ = 7.5 Hz, 3H. Si-Me), 2.0, 1.2, 0.7 (t, m, t, 18H, Bu), 6.0 (dd, 1H, $^2J(^1H,^1H)$ = 4.6 Hz, $^3J(^1H,^1H)$ = 13.4 Hz, H_2C=), 6.1 (dd, 1H, $^2J(^1H,^1H)$ = 4.4 Hz, $^3J(^1H,^1H)$ = 20.0 Hz, H_2C=), 6.2 (dd, 1H, $^3J(^1H,^1H)_{cis}$ = 13.5 Hz, $^3J(^1H,^1H)_{trans}$ = 20.0 Hz, Si-HC=).

19c: ^1H NMR (400 MHz): δ = 0.5 (s, $^2J(^1H,^{29}Si)$ = 7.6 Hz, 3H, Si-Me), 6.0 (dd, 1H, $^2J(^1H,^1H)$ = 4.6 Hz, $^3J(^1H,^1H)$ = 13.2 Hz, H_2C=), 6.2 (dd, 1H, $^2J(^1H,^1H)$ = 4.6 Hz, $^3J(^1H,^1H)$ = 20.1 Hz, H_2C=), 6.3 (dd, 1H, $^3J(^1H,^1H)_{cis}$ = 13.1 Hz, $^3J(^1H,^1H)_{trans}$ = 20.1 Hz, Si-HC=), 6.9 - 7.4 (m, 10H, Ph).

20a: ^1H NMR (400 MHz): δ = 1.9, 1.2, 0.6 (t, m, t, 18H, Bu), 6.0 (dd, 1H, $^2J(^1H,^1H)$ = 4.6 Hz, $^3J(^1H,^1H)$ = 13.4 Hz, H_2C=), 6.1 (dd, 1H, $^2J(^1H,^1H)$ = 4.6 Hz, $^3J(^1H,^1H)$ = 20.1 Hz, H_2C=), 6.2 (dd, 1H, $^3J(^1H,^1H)_{cis}$ = 13.2 Hz, $^3J(^1H,^1H)_{trans}$ = 20.1 Hz, = Si-HC=), 7.9, 7.1 (m, m, 5H, Si-Ph).

20c: ^1H NMR (400 MHz): δ = 6.2 (m, 2H, H_2C=), 6.0 (m, 1H, Si-HC=), 7.3, 6.8 - 6.9 (m, m, 15H, Si-Ph, Ph).

21c: ^1H NMR (400 MHz): δ = 0.5 (s, 3H, Si-Me), 1.9 (d, 2H, $^3J(^1H,^1H)$ = 7.8 Hz, Si-CH_2), 5.0, 5.1 (m, 2H, $J(^1H,^1H)$ = 11.6, 18.7 Hz, H_2C=), 6.0 (m, 1H, =CH), 7.4, 6.9 (m, m, 10H, Ph).

22a: ^1H NMR (400 MHz): δ = 2.0, 1.3, 0.7 (t, m, t, 18H, Bu), 6.0 (m, 6H, Si-vinyl).

22c: ^{1}H NMR (400 MHz): δ = 6.0 (t, 2H, $^{3}J(^{1}H,^{1}H)$ = 8.8 Hz, Si-HC=), 6.2 (d, 4H, =CH_2), 7.3, 6.9 (m, m, 10H, Ph).

22e: ^{1}H NMR (400 MHz): δ = 7.3, 7.1, 1.1 (m, m, s, 26H, 4-^{t}Bu-C_6H_4), 6.1 (dd, 2H, Si-HC=), 6.3 (m, 4H, =CH_2).

23a: ^{1}H NMR (400 MHz): δ = 1.9, 1.2, 0.6 (t, m, t, 9H, Bu), 6.0 (dd, 2H, Si-HC=), 6.2 (m, 4H, =CH_2), 7.3, 7.0, 1.0 (m, m, s, 13H, 4-^{t}Bu-C_6H_4).

10.4.1.5. *Syntheses of trialkyn-1-ylsilane derivatives **24** and **25.***

The trichloro(methyl)silane (10 mmol, 1.3 mL) was slowly added to freshly prepared suspension of hexynyl lithium (30 mmol), at -78 °C in hexane. The work up procedure was exactly the same as described for the above silanes **11a - c**. The products after removal of all volatile materials were oily (**24a**, **25a**) or solid crystalline materials (**24c**, **25c**, **d**). They were also isolated from reaction mixture accompanied by silanes **5**, **6** and **16**, **17**.

24a: ^{1}H NMR (400 MHz): δ = 0.6 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 7.3 Hz, Si-Me), 1.9, 1.2, 0.7 (t, m, t, 27H, Bu).

24c: ^{1}H NMR (400 MHz): δ = 0.8 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 7.8 Hz, Si-Me), 7.6, 7.5 (m, m, 15H, Ph).

25a: ^{1}H NMR (400 MHz): δ = 2.2, 1.4, 1.3, 0.8 (t, m, m, t, 27H, Bu), 7.7, 7.3 (m, m, 5H, Si-Ph).

25c: ^{1}H NMR (400 MHz): δ = 7.9, 7.2 - 7.5 (m, m, 20H, Ph, Si-Ph).

25d: ^{1}H NMR (400 MHz): δ = 7.2, 6.7, 1.9 (m, m, s, 21H, 4-Me-C_6H_4), 7.8, 7.5 (m, m, 5H, Si-Ph).

10.4.1.6. *Preparation of tetraalkyn-1-ylsilane derivatives **26b - d***

Tetrachlorosilane (10 mmol, 1.2 mL) was added slowly at low temperature (-78 °C) to a freshly prepared suspension of Li-C≡C-(4-Me-C_6H_4) (41 mmol, in hexane). The reaction mixture was allowed to warm up to room temperature. Then the mixture was heated to 40 °C for 2 h. The solid was washed with plenty of toluene before separation. All volatiles were removed under reduced pressure. The residue left behind mainly contained $Si(C{\equiv}C\text{-}(4\text{-}Me\text{-}C_6H_4))_4$ (**26d**, solid crystalline) and other expected fractions, $Cl_3Si(C{\equiv}C(4\text{-}Me\text{-}C_6H_4))$, $Cl_2Si(C{\equiv}C\text{-}(4\text{-}Me\text{-}C_6H_4))_2$ and $ClSi(C{\equiv}C\text{-}(4\text{-}Me\text{-}C_6H_4))_3$ in small quantity (ca. 10 %). Fortunately these fractions (side products) were soluble in hexane and were separated from the solid by washing it 3 to 4 times

with hexane. The solid was dissolved in THF and single crystals suitable for X-ray diffraction studies were obtained at room temperature. The synthetic procedure and work up was the same for the silane **26b**. The silane **26c** was obtained as solid from the mixture containing silane **7c**.

26b: ^{1}H NMR (400 MHz): δ = 1.1 (s, 36H, ^{t}Bu).

26c: ^{1}H NMR (400 MHz): δ = 7.4, 7.1 (m, m, 20H, Ph).

26d: M. p. = decomposes above 263 °C; ^{1}H NMR (400 MHz): δ = 7.6, 7.3, 2.4 (m, m, s, 28H, 4-Me-C_6H_4).

*10.4.2. Hydroboration of alkyn-1-ylsilanes **1 - 26**.*

10.4.2.1. *Hydroboration of monoalkyn-1-ylsilanes **4 - 7** using BEt_3 as hydroborating reagent.*

An NMR tube was charged with dichloro(phenylethynyl)silane **4c** (0.37g, 1.8 mmol) and BEt_3 (in excess). The tube was sealed and kept at 110 – 120 °C for 3 d. The reaction was monitored from time to time by ^{29}Si NMR. After the reaction was complete, the NMR tube was cooled in liquid nitrogen, opened carefully, warmed to room temperature and the contents were transferred to a Schlenk tube. All the volatiles were removed in a vacuum and the oily compound left was identified as **27c** (yield 80 %). The analogous procedure was adopted for the synthesis of **28** and **29** (except for the reaction time); **28a**, **28c** (14 d), **29a**, **29c** (20 d), **29b** (30 d; only 40 % of the reactants were converted into products), **30a** (24 d), **30c** (28 d).

27c: ^{1}H NMR (400 MHz): δ = 0.9, 1.4 (t, m, 6H, 4H, BEt_2), 5.6 (s, 1H, $^{1}J(^{1}H,^{29}Si)$ = 292.4 Hz, Si-H), 6.9 - 7.1 (m, 5H, 1H, Ph, =C-H)

28a: ^{1}H NMR (400 MHz): δ = 0.7 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 7.4 Hz, Si-Me), 1.0, 1.2 (t, m, 10H, BEt_2), 0.8, 1.1, 2.2 (t, m, m, 9H, Bu), 5.9 (t, 1H, $^{3}J(^{1}H,^{29}Si)$ = 26.7 Hz, $^{3}J(^{1}H,^{1}H)$ = 7.4 Hz, =CH); EI-MS: m/z (%) = 265 (36) [M^+], 250 (11) [M^+-Me], 229 (27) [M^+-Cl], 207 (15) [M^+-Bu], 196 (10) [M^+-BEt_2], 151 (12) [M+-Si(Me)Cl_2], 43 (87) [$C_3H_7^+$], 41 (100) [$C_3H_5^+$].

28c: ^{1}H NMR (400 MHz): δ = 0.3 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 8.6 Hz, Si-Me), 0.8, 1.2 (t, m, 10H, BEt_2), 6.8 - 7.0 (m, 5H, Ph), 6.7 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 26.3 Hz, =CH). EI-MS: m/z (%) = 285(29) [M^+], 270 (35) [M^+-CH_3], 257 (30) [M^+-C_2H_5], 216 (11) [M^+- BEt_2], 207 (69), 171 (27) [M^+-$MeSiCl_2$], 113 (82), 102 (32), 103 (47), 91 (100).

29a: ^{1}H NMR (400 MHz): δ = 0.4, 0.8 - 1.1, 2.1 (t, m, m, 9H, Bu), 0.8, 0.8 - 1.1 (t, m, 10H, BEt_2), 5.8 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.4 Hz, $^{3}J(^{1}H,^{29}Si)$ = 24.3 Hz, =CH), 6.8 - 7.5 (m, 5H, Si-Ph). EI-MS: m/z (%) = 326 (5) [M^+], 325 (15) [M^+ - H], 310 (12) [M^+ - CH_4], 298 (8) [M^+-C_2H_5], 291 (6) [M^+ - Cl], 256 (4), 199 (10), 221 (100), 175 (32), 141 (85), 139 (70).

29a´: ^{1}H NMR (400 MHz): δ = 0.4, 0.8 - 1.1, 1.8 (t, m, m, 9H, Bu), 0.6, 0.8 - 1.1 (t, m, 10H, BEt_2), 5.6 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.4 Hz, =CH), 6.8 - 7.5 (m, 5H, Si-Ph).

29b: ^{1}H NMR (400 MHz): δ = 0.9 (s, 9H, ^{t}Bu); 1.0, 1.4 (t, m, 10H, BEt_2), 7.0, 7.7 (m, 10H, Si-Ph), 6.1 (s, 1H, $^{3}J(^{29}Si,^{1}H)$ = 30.8 Hz, =CH).

29c: ^{1}H NMR (400 MHz): δ = 1.1, 1.5 (t, m, 10H, BEt_2), 6.8 - 7.8 (m, 10H, 1H, Si-Ph, Ph, =CH); EI-MS: m/z (%) = 347 (5) [M^+], 346 (9) [M^+ - H], 332 (8) [M^+ - CH_4], 316 (32) [M^+ - C_2H_5], 317 (79) [M^+ - C_2H_6], 278 (15) [M^+ - BEt_2], 271 (74) [M^+ - C_6H_6], 270 (13) [M^+ - C_6H_5], 178 (100) [$C_8H_8BClSi^+$], 171 (12) [M^+ - $SiCl_2Ph$].

30a: ^{1}H NMR (400 MHz): δ = 1.0, 1.1, 1.8, 2.3 (t, m, m, t, 9H, Bu), 0.7, 1.3 (t, m, 10H, BEt_2), 6.0 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.4 Hz, $^{3}J(^{1}H,^{29}Si)$ = 35.3, =CH).

30a´: ^{1}H NMR (400 MHz): δ = 1.0, 1.1, 1.8, 2.4 (t, m, m, t, Bu), 0.8, 1.3 (t, m, 10H, BEt_2), 6.6 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.5 Hz, =CH); MS: *m/z* (%) = 285 (10) [M^+], 207 (20), 115 (20), 92 (100), 27 (95).

30c: ^{1}H NMR (400 MHz): δ = 0.9, 1.3 (t, m, 10H, BEt_2), 6.9 - 7.3 (m, 6H, Ph, $^{3}J(^{1}H,^{29}Si)$ = 35.8 Hz (measured from ^{29}Si NMR data), =CH).

30c´: ^{1}H NMR (400 MHz): δ = 0.8, 1.2 (t, m, BEt_2), 7.7 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 32.9 Hz, =CH), 6.9 - 7.3 (m, 5H, Ph); MS: *m/z* (%) = 304 (9) [M^+], 275 (35) [M^+ - C_2H_5], 269 (6) [M^+ - Cl], 265 (100), 240 (16), 236 (31). 199 (29), 133 (13).

10.4.2.2. *Hydroboration of monoalkyn-1-ylsilanes **5 - 7** using BPr_3 as hydroborating reagent*

A mixture of alkyny-1-ylsilanes **5a** (0.50 g, 2.6 mmol), an excess of tripropylborane, BPr_3 and few drops of C_6D_6 was sealed in an NMR tube. The reaction mixture was heated to 80 - 100 °C. The progress of the reaction was monitored by ^{29}Si NMR spectroscopy. 1,2-Hydroboration reaction was complete after 2 d, The NMR tube was cooled in liquid N_2, opened, warmed to room temperature and all volatile materials were removed under reduced pressure. The product was identified as a mixture of **31a** and **31a´**. The procedure for other compounds was

exactly the same except that the heating period was different for each reaction, **31c**, **32a**, **32c** (5 d), **33a** (2 d) and **33c** (6 d).

31a: ^{1}H NMR (400 MHz): δ = 0.7 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 7.4 Hz, Si-Me), 0.8, 1.3 - 1.5, 2.2 (t, m, m, 9H, Bu), 0.9, 1.3 - 1.5 (t, m, 14H, BPr_2), 6.0 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.5 Hz, $^{3}J(^{1}H,^{29}Si)$ = 34.7 Hz, =CH).

31a´: ^{1}H NMR (400 MHz): δ = 0.6 (s, 3H, Si-Me), 0.8, 1.3 - 1.5, 2.4 (t, m, m, 9H, Bu), 1.0, 1.3 - 1.5 (t, m, 14H, BPr_2), 6.5 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.5 Hz, $^{3}J(^{1}H,^{29}Si)$ = 32.7 Hz, =CH).

31c: ^{1}H NMR (400 MHz): δ = 0.4 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 7.5 Hz, Si-Me), 1.0, 1.4, 1.6 (t, m, m, 14H, BPr_2), 6.9 - 7.4 (m, 6H, Ph, =CH).

31c´: ^{1}H NMR (400 MHz): δ = 0.38 (s, 3H, Si-Me), 1.0, 1.4, 1.6 (t, m, m, 14H, BPr_2), 6.9 - 7.4 (m, 6H, Ph, =CH).

32a: ^{1}H NMR (400 MHz): δ = 0.5, 1.0 - 1.4, 2.0 (t, m, m, 9H, Bu), 0.8, 1.0 - 1.4 (m, t, 14H, BPr_2), 6.9 - 7.6 (m, 5H, Si-Ph), 5.9 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.4 Hz, =CH).

32a´: ^{1}H NMR (400 MHz): δ = 0.5, 1.0 - 1.4, 2.1 (t, m, m, 9H, Bu), 0.7, 1.0 - 1.4 (t, m, 14H, BPr_2), 6.9 - 7.6 (m, 5H, Si-Ph), 5.8 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.4 Hz, =CH).

32c: ^{1}H NMR (400 MHz): δ = 0.9, 1.5, (t, m, 14H, BPr_2), 6.8 - 7.2, 7.4 (m, m, 10H, 1H, Ph, Si-Ph, =CH).

33a: ^{1}H NMR (400 MHz): δ = 0.9, 1.2 - 1.3, 1.4 (t, m, m, 14H, BPr_2), 0.8, 1.2 - 1.3, 2.4 (t, m, m, 9H, Bu), 6.1 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.4 Hz, $^{3}J(^{1}H,^{29}Si)$ = 35.0 Hz, =CH).

33c: ^{1}H NMR (400 MHz): δ = 0.9, 1.1, 1.4 (t, m, t, 14H, BPr_2), 6.9 - 7.4 (m, 6H, Ph, =CH).

10.4.2.3. *Hydroboration of monoalkyn-1-ylsilanes **1 - 7** using 9-BBN as hydroborating reagent*

Pure **1a** (1.01 g, 4.51 mmol) was dissolved in toluene (10 mL) and 9-BBN (0.56 g, 4.51 mmol) was added as a solid in one portion. The reaction mixture was heated to reflux for 30 min, the solvent was removed in *vacuo*, and the remaining colorless oil was identified as a mixture of **34a** and **34a´**. The same reaction was carried out at r. t. in toluene as well as in THF as solvents, and the same results were obtained except that the reaction time was long (ca. 12 h). The procedure for the preparation of other alkenylsilane derivatives **34** - **40** was exactly the same. The heating period of the reactions lasted 0.5 - 3 h. In case of **40a**, the reaction was carried out at the same

temperature in a sealed NMR tube using benzene as the solvent, and the reaction was completed after 1 h.

34a: ^{1}H NMR (300 MHz): δ = 1.0, 1.3 - 1.6, 2.4 (t, m, m, 9H, Bu), 1.4 - 1.8 (m, 14H, 9 - BBN), 5.1 (s, 1H, $^{1}J(^{1}H,^{29}Si)$ = 205.3 Hz, Si-H), 7.3 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.1 Hz, =CH), 7.4 - 7.8 (m, 5H, Si-Ph).

34a´: ^{1}H NMR (300 MHz): δ = 0.9, 1.3 - 1.6, 2.5 (m, m, t, 9H, Bu), 1.4 - 1.8 (m, 14H, 9-BBN), 5.2 (s, 1H, $^{1}J(^{1}H,^{29}Si)$ = 189.6 Hz, Si-H), 7.1 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.1 Hz, =CH), 7.4 - 7.8 (m, 5H, Si-Ph).

34c: ^{1}H NMR (300 MHz): δ = 1.5 - 1.9 (m, 14H, 9-BBN), 5.5 (s, 1H, $^{1}J(^{1}H,^{29}Si)$ = 237.5 Hz, Si-H) 7.2–7.6 (m, 10H, Si-Ph, Ph), 8.2 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 20.4 Hz, =CH).

35a: ^{1}H NMR (300 MHz): δ = 0.6 (s, 3H, Si-Me), 0.7, 1.3, 1.4, 2.2 (t, m, m, m, 9H, Bu), 1.5 - 1.8 (m, 14H, 9-BBN), 6.9 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.2 Hz, =CH), 7.2–7.6 (m, 5H, Si-Ph).

35c: Yield after recrystallization from pentane at r. t. = 75 %; m. p. = 58–60 °C; ^{1}H NMR (300 MHz): δ = 0.3 (s, 3H, Si-Me), 1.5 - 1.9 (m, 14H, 9-BBN), 8.0 (s, $^{3}J(^{1}H,^{29}Si)$ = 20.3 Hz, =CH), 7.0 - 7.4 (m, 10H, Si-Ph, Ph).

36a: ^{1}HNMR (300 MHz): δ = 0.7, 1.0, 1.2, 2.2 (t, m, m, m, 9H, Bu), 1.3 - 1.9 (m, 14H, 9-BBN), 7.2 (t, 1H, ^{3}J ($^{1}H,^{1}H$) = 7.4 Hz, =CH), 7.1 - 7.7 (m, 10H, $SiPh_2$).

36c: ^{1}H NMR (300 MHz): δ = 1.1–1.7 (m, 14H, 9-BBN), 6.8–7.5 (m, 15H, $SiPh_2$, Ph), 8.1 (s, $^{3}J(^{1}H,^{29}Si)$ = 20.5 Hz, =CH).

37c: Yield after recrystallization = 91 %; m. p. = 42 - 45 °C; ^{1}H NMR (400 MHz): δ = 1.4 - 2.2 (m, 14H, 9-BBN), 5.8 (s, 1H, $^{1}J(^{1}H,^{29}Si)$ = 289.2 Hz, Si-H), 7.2, 7.4 (m, m, 5H, Ph), 8.1 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 25.9 Hz, =CH).

38a: ^{1}H NMR (400 MHz): δ = 0.6 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 7.5 Hz, Si-Me), 1.3 - 1.9 (m, 14H, 9-BBN), 0.8, 1.1 - 1.3, 2.4 (t, m, m, 9H, Bu), 7.0 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.2 Hz, $^{3}J(^{1}H,^{29}Si)$ = 25.5 Hz, =CH); EI-MS: m/z (%) = 317 (35) [M^+], 316 (91) [M^+ - H], 281 (5) [M^+ - Cl], 274 (22) [M^+ - C_3H_7], 260 (12) [M^+ - Bu], 113 (63), 110 (43), 67 (100).

38c: ^{1}H NMR (400 MHz): δ = 0.1 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 7.3 Hz, Si-Me), 1.1 - 1.9 (m, 14H, 9-BBN), 7.6 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 25.6 Hz, =CH), 6.8 - 7.1 (m, 5H, Ph); EI-MS: m/z (%) = 337 (37) [M^+], 336 (99) [M^+ - H], 258 (41), 223 (100) [M^+ - $MeSiCl_2$], 216 (71) [M^+ - $C_8H_{14}B$], 201 (44), 181 (28), 165 (52), 138 (37), 113 (18) [$Si(Cl)_2Me^+$].

39a: ^{1}H NMR (300 MHz): δ = 0.5, 1.0, 1.1, 2.1 (t, m, m, m, 9H, Bu), 1.4 - 1.6 (m, 14H, 9-BBN), 6.9 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.5 Hz, =CH), 7.1 - 7.5 (m, 5H, Si-Ph).

39b: ^{1}H NMR (400 MHz): δ = 1.1 (s, 9H, ^{t}Bu), 1.3 - 1.9 (m, 14H, 9-BBN), 7.0 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 29.5 Hz, =CH), 7.1, 7.7 (m, m, 5H, Si-Ph).

39c: Yield after recrystalization from hexane/chloroform (4:1) at r. t. = 80 %; m. p. 74–75 °C; ^{1}H NMR (300 MHz): δ = 1.0 - 2.0 (m, 14H, 9-BBN), 7.8 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 25.7 Hz, =CH), 6.8 - 7.4 (m, 10H, Si-Ph, Ph).

40a: ^{1}H NMR (300 MHz): δ = 0.8, 1.1 - 1.3, 2.5 (t, m, m, 9H, Bu), 1.3 - 1.9 (m, 14H, 9-BBN), 7.0 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.8 Hz, =CH); EI-MS: m/z (%) = 336 (28) [M^{+}], 279 (7) [M^{+}–C_4H_9], 266 (5), 135 (8), 110 (100), 82 (65).

40c: ^{1}H NMR (300 MHz): δ = 1.3–2.0 (m, 14H, 9-BBN), 7.8 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 33.2 Hz, =CH), 6.9 - 7.2 (m, 5H, Ph); EI-MS: m/z (%) = 256 (1) [M^{+}], 236 (23) [M^{+}–$C_8H_{14}B$], 103 (100), 110 (32), 82 (48).

10.4.2.4. *Hydroboration of alkyn-1-yl(dichloro)(vinyl)silanes **10a** and **10c** using BEt_3 and BPr_3*

The silane **10a** (1.30 g, 6 mmol) was dissolved in an excess of BEt_3 (2.5 mL, 18 mmol) and the solution was heated to 120 °C for 7 d. After the reaction was almost complete all volatiles were removed under reduced pressure and the oily liquid left was identified as **41a** by NMR spectroscopy. The same procedure was adopted for the preparation of **41c** and **42c**, except that heating lasted for 10 d and 8 d, respectively.

41a: ^{1}H NMR (400 MHz): δ = 0.9, 1.3, 1.9, 2.2 (t, m, m, t, 9H, Bu), 0.7, 1.2 (m, t, 10H, BEt_2), 6.0 (t, 1H, =CH), 5.9 (dd, 1H, $^{2}J(^{1}H,^{1}H)$ = 3.9 Hz, $^{3}J(^{1}H,^{1}H)_{cis}$ = 13.1 Hz, =CH_2), 6.0 (dd, 1H, $^{3}J(^{1}H,^{1}H)_{cis}$ = 13.1 Hz, $^{3}J(^{1}H,^{1}H)_{trans}$ = 19.5 Hz, Si-CH), 6.1 (dd, 1H, $^{2}J(^{1}H,^{1}H)$ = 4.0 Hz, $^{3}J(^{1}H,^{1}H)_{trans}$ = 19.5 Hz, =CH_2).

41c: ^{1}H NMR (400 MHz): δ = 0.8, 1.2 (t, m, 10H, BEt_2), 5.4 (dd, 1H, $^{2}J(^{1}H,^{1}H)$ = 3.1 Hz, $^{3}J(^{1}H,^{1}H)_{cis}$ = 14.1 Hz, =CH_2), 5.5 (dd, 1H $^{3}J(^{1}H,^{1}H)_{cis}$ = 14.0 Hz, $^{3}J(^{1}H,^{1}H)_{trans}$ = 19.6 Hz, Si-CH), 5.6 (dd, 1H, $^{2}J(^{1}H,^{1}H)$ = 3.1 Hz, $^{3}J(^{1}H,^{1}H)_{trans}$ = 19.6 Hz, =CH_2), 6.8 - 7.1 (m, 6H, Ph, =CH).

42c: ^{1}H NMR (400 MHz): δ = 0.9, 1.4 - 1.5 (t, m, 14H, BPr_2), 5.6 - 6.0 (m, Si-CH=CH_2), 6.9 - 7.2 (m, 6H, Ph, =CH).

10.4.2.5. *Hydroboration of chloro(vinyl)silanes **S9** and **S11** with BEt_3, BPr_3 and 9-BBN*

The trichloro(vinyl)silane, **S9** (4.00 g, 26.9 mmol) was given into a pressure-safe Schlenk tube, an excess of BEt_3 (6 mL, 44 mmol) was added and the mixture was heated at 120 °C for 3 d. A dark color developed and black solid materials were formed. After removing the volatiles in a vacuum, the remaining liquid (yield 25 %) was separated from the solid and analysed by NMR spectroscopy as a mixture of **43** and **43´**, with the latter in slight excess. The same procedure was applied to the synthesis of **46** and **46´** and the analogous behaviour was observed in the course of heating. The reaction for the synthesis of **44**, **44´** and **47** starting from BPr_3 and **S9** and **S10**, respectively, was carried out at 100 °C for 5 d and decomposition was not observed. In contrast, 9-BBN in THF reacts at r. t. after 2 h with **S9** and **S10** to give selectively **45** and **48**.

43, **43´**: ^{1}H NMR (400 MHz): δ = 0.4, 0.4 (s, s, 3H, 3H, Si-Me), 0.9, 1.3 (t, m, BEt_2, CH_3, CH_2CH_2), 1.7 (q, $^3J(^1H,^1H)$ = 7.4 Hz, 1H, CH).

44, **44´**: ^{1}H NMR (400 MHz): δ = 0.5, 0.5 (s, s, 3H, 3H, Si-Me), 0.9 - 1.0, 1.1 - 1.2, 1.3 - 1.4 (m, m, m, BPr_2, Si-CH_2-CH_2, CH_3), 1.7 (q, 1H, CH).

45: ^{1}H NMR (400 MHz): δ = 0.5 (s, 3H, $^2J(^1H,^{29}Si)$ = 7.3 Hz, Si-Me), 1.0, 1.4 (m, m, 4H, Si-CH_2-CH_2), 1.6 - 1.8 (m, 14H, 9-BBN).

46: ^{1}H NMR (400 MHz): δ = 0.9, 1.2 (t, m, 10H, BEt_2), 1.9 (q, 1H, Si-CH), 1.1 (d, 3H, CH_3).

47: B. p. 38 °C/0.1 Torr (ca. 90 % pure); ^{1}H NMR (400 MHz): δ = 0.9, 1.5 (t, m, CH_3, CH_2, BPr_2), 1.2 (d, 3H, $^3J(^1H,^1H)$ = 7.0 Hz, CH_3), 1.9 (q, 1H, CH).

48: ^{1}H NMR (400 MHz): δ = 1.1 - 1.8 (m, 14H, 9-BBN), 1.4, 1.2 (m, m, 4H, CH_2, $Si(CH_2)_2$).

10.4.2.6. *Hydroboration of dialkyn-1-ylsilanes **14a** and **16 - 18** using 9-BBN*

An NMR tube was charged with a solution of the silane **14a** (0.74 g, 2.2 mmol) in C_6D_6 (1.5 mL) and 9-BBN (0.27 g, 2.2 mmol) was added as a solid in one portion. The mixture was heated to 80 °C for 20 min. In this time 9-BBN was completely consumed (^{11}B NMR spectra). By analysing the product, compound **51a** was identified from its characteristic NMR data. The reactions of silanes **16 - 18** were conducted in the same way. In two cases, side reactions afford silanes **49a** and **50a**, in which 1,2-hydroboration of both the Si-C≡C- bonds has taken place.

49a: ^{1}H NMR (400 MHz): δ = 0.6 (s, 3H, Si-Me), 0.8, 1.3, 2.4 (t, m, m, 18H, Bu), 1.3, 1.9-2.0 (m, m, 28H, 9-BBN), 6.8 (t, 2H, $^{3}J(^{1}H,^{1}H)$ = 7.2 Hz, $^{3}J(^{1}H,^{29}Si)$ = 19.4 Hz, =CH).

50a: ^{1}H NMR (400 MHz): δ = 0.8, 1.3, 2.5 (t, m, m, 18H, Bu), 1.3 - 2.1 (m, 28H, 9-BBN), 6.9 (t, 2H, $^{3}J(^{1}H,^{1}H)$ = 7.5 Hz, =CH).

51: ^{1}H NMR (400 MHz): δ = 0.6, 1.0, 1.1 - 1.2, 2.2, (t, m, m, m, 9H, =C-Bu), 0.6, 1.1 - 1.2, 1.9 (t, m, m, 9H, ≡C-Bu), 1.5 - 1.8 (m, 14H, 9-BBN), 7.1 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.2 Hz, =CH), 7.0 - 7.1, 7.7 (m, m, 10H, $SiPh_2$).

52a: ^{1}H NMR (400 MHz): δ = 0.7 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 7.4 Hz, Si-Me), 0.7, 0.9, 1.2 - 1.3, 2.0, 2.5 (t, t, m, t, m, 18H, Bu), 1.4, 1.8 - 2.0 (m, m, 14H, 9-BBN), 7.0 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.3 Hz, $^{3}J(^{1}H,^{1}H)$ = 21.1 Hz, =CH).

52c: ^{1}H NMR (400 MHz): δ = 0.3 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 7.7 Hz, Si-Me), 1.2, 1.6 - 2.1 (m, m, 14H, 9-BBN), 7.3, 7.1, 7.0, 6.7 - 6.8 (m, m, m, m, 10H, Ph), 7.9 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 21.7 Hz, =CH).

53c: ^{1}H NMR (400 MHz): δ = 1.4, 1.9 - 2.2 (m, m, 14H, 9-BBN), 7.9, 7.6, 6.9 - 7.3 (m, m, m, 15H, Si-Ph, Ph), 8.2 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 21.4 Hz, =CH).

54a: ^{1}H NMR (400 MHz) δ = 0.6, 0.8, 1.1, 1.3, 1.8, 2.7 (t, t, m, m, m, m, 18H, Bu), 1.3 - 2.1 (m, 14H, 9-BBN), 7.1 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.5 Hz, =CH).

10.4.2.7. *Reaction of alkenyl(chloro)silanes **34 - 36** with alkyn-1-yl lithium to afford borates **55a**, **56c** and(or) alkyn-1-ylsilanes **57 - 61**.*

To a freshly prepared suspension of Li-C≡C-Ph in hexane (10 mL) at –78 °C the silane **35c** (0.68 g, 1.79 mmol) was added. The reaction mixture was warmed to room temperature and kept stirring for 3 h. Then solid materials were separated and the solvent was removed in *vacuo*. A colorless oily liquid was left behind identified as **57c.** The alkenyl(alkyn-1-yl)silanes **58 - 61** were prepared in the same way. In case of **36a** and **35c** the desired products were accompanied by borate-like intermediates **55a** and **56c**, respectively. These compounds were found to rearrange into final products *via* -C≡C- bond migration from boron to silicon and LiCl elimination.

55a: ^{1}H NMR (300 MHz): δ = 0.7, 0.7 - 0.9, 2.1 (t, m, m, 9H, Bu), 1.0 - 1.7 (m, 14H, 9-BBN). 7.2 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.3 Hz, =CH), 6.8 - 7.7 (m, 15H, $SiPh_2$, Ph).

56c: ^{1}H NMR (400 MHz): δ = 0.03 (s, 9H, $SiMe_3$), 0.3 (s, 3H, Si-Me), 1.1 - 2.0 (m, 14H, 9-BBN), 6.9 - 7.6 (m, 10H, Si-Ph, Ph), 8.0 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 17.6 Hz, =CH).

57a: ^{1}H NMR (400 MHz): δ = 0.6 (s, 3H, Si-Me), 0.8, 1.2 - 1.8, 2.4 (t, m, m, 9H, Bu), 1.2 - 1.8 (m, 14H, 9-BBN), 7.0 (t, 1H, =CH), 7.2 - 7.7 (m, 10H, Ph, Si-Ph).

57c: ^{1}H NMR (400 MHz): δ = 0.1 (s, 3H, Si-Me), 1.0 - 1.5 (m, 14H, 9-BBN), 6.5 - 7.4 (m, 15H, Si-Ph, Ph), 7.8 (s, 1H, =CH).

58a: ^{1}H NMR (400 MHz): δ = 0.5, 0.7 - 0.9, 2.3 (t, m, m, 9H, Bu), 1.0 - 1.7 (m, 14H, 9-BBN), 7.1 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.2 Hz, =CH), 6.8 - 7.7 (m, 15H, $SiPh_2$, Ph).

58c: ^{1}H NMR (400 MHz): δ = 1.3 - 1.8 (m, 14H, 9-BBN), 6.6 - 7.8 (m, 20H, $SiPh_2$, Ph), 8.1 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 17.8 Hz, =CH).

59c: ^{1}H NMR (400 MHz): δ = -0.1 (s, 9H, $SiMe_3$), 1.2–2.0 (m, 14H, 9-BBN), 5.3 (s, 1H, $^{1}J(^{1}H,^{29}Si)$ = 211.3 Hz, Si-H), 8.1 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 17.7 Hz, =CH), 6.8 - 7.6 (m, 10H, Si-Ph, Ph).

60a: ^{1}H NMR (400 MHz): δ = -0.04 (s, 9H, $SiMe_3$), 0.5 (s, 3H, Si-Me), 0.6, 1.0, 1.2, 2.3 (t, m, m, m, 9H, Bu), 1.2 - 1.8 (m, 14H, 9-BBN), 6.9 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.3 Hz, =CH), 7.0 - 7.8 (m, 5H, Si-Ph).

60c: ^{1}H NMR (400 MHz): δ = 0.03 (s, 9H, $SiMe_3$), 0.3 (s, 3H, Si-Me), 1.1 - 2.0 (m, 14H, 9-BBN), 6.9 - 7.6 (m, 10H, Si-Ph, Ph), 8.0 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 15.8 Hz, =CH).

61a: ^{1}H NMR (400 MHz): δ = 0.2 (s, 9H, $SiMe_3$), 0.8, 0.9 - 1.3, 2.3 (t, m, m, 9H, Bu), 1.3 - 1.8 (m, 14H, 9-BBN), 7.2 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.6 Hz, =CH), 7.3 - 7.6 (m, 10H, $SiPh_2$).

61c: ^{1}H NMR (400 MHz): δ = 0.03 (s, 9H, $SiMe_3$), 1.3–2.6 (m, 14H, 9-BBN), 6.9–7.8 (m, 15H, $SiPh_2$, Ph), 8.3 (s, 1H $^{3}J(^{1}H,^{29}Si)$ = 22.3 Hz, =CH).

10.4.2.8. *Hydroboration of trialkyn-1-ylsilanes **24** and **25** using* 9-BBN

A Schlenk tube was charged with a solution of silane **24a** (0.45 g, 1.57 mmol) and 9-BBN (0.19 g, 1.56 mmol) in THF. The reaction mixture was stirred at room temperature for 12 h. After the reaction was complete, all volatile materials were removed under reduced pressure and the oily liquid left was identified as the mixture of alkenylsilanes **62a** and **66a** (in the ratio of 8:2, respectively, from ^{1}H NMR). The other members of this series (**63** and **67**) were synthesized at high temperature (80 - 100 °C) using toluene or benzene as the solvent. The reaction period lasted from 10 - 30 minutes. Compound **65** was prepared in a different way. A solution of alkenylsilane **29c** (1.86 g, 5.37 mmol) in hexane (5 mL) was added to freshly prepared 3,3-dimethylbutynyl lithium at -78 °C. The reaction mixture was allowed to warm up to room temperature slowly. After stirring at room temperature for three

hours all the volatiles were removed in a vacuum, and solid materials were separated, and the oily liquid left was identified as the mixture of **64** and **65**. Both compounds can readily be identified from their characteristic ^{29}Si chemical shifts.

62a: ^{1}H NMR (400 MHz): δ = 0.6 (s, 3H, Si-Me), 0.7, 0.9, 1.9 - 1.5, 1.9, 2.6 (t, t, m, m, t, 27H, Bu), 1.4, 1.8 - 2.1 (m, 14H, 9-BBN), 7.0 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.2 Hz, =CH).

62c: ^{1}H NMR (400 MHz): δ = 0.4 (s, 3H, Si-Me), 1.2–2.2 (m, 14H, 9-BBN), 6.7 - 7.2, 7.5 (m, m, 15H, Ph), 8.0 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 18.8 Hz, =CH).

63a: ^{1}H NMR (400 MHz): δ = 0.7, 0.8, 1.9 - 1.5, 2.6 (t, t, m, m, 27H, Bu), 1.4 - 2.1 (m, 14H, 9-BBN), 7.2, 7.7 (m, 6H, Si-Ph, =CH).

63c: ^{1}H NMR (400 MHz): δ = 1.2 - 1.9 (m, 14H, 9-BBN), 6.6 - 7.9 (m, 20H, Si-Ph, Ph), 8.0 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 22.1 Hz, =CH).

63d: ^{1}H NMR (400 MHz): δ = 1.3 - 2.0 (m, 14H, 9-BBN), 1.9, 1.9, 2.0, 6.4 - 8.2 (s, s, s, m, 27H, Si-Ph, 4-Me-C_6H_4, =CH).

64c: proposed on the basis of ^{29}Si NMR data (-42.5 ppm, Figure 3.9).

65c: ^{1}H NMR (400 MHz): δ = 0.8 (s, 18H, ^{t}Bu), 1.0, 1.6 (t, m, 10H, BEt_2), 6.9 - 7.7 (m, 11H, Si-Ph, Ph, =CH).

66a: ^{1}H NMR (400 MHz): δ = 0.6 (s, 3H, Si-Me), 0.7, 0.9, 1.9 - 1.5, 2.4 (t, t, m, m, 27H, Bu), 1.4, 1.8 - 2.1 (m, 28H, 9-BBN), 6.9 (t, 2H, $^{3}J(^{1}H,^{1}H)$ = 7.1 Hz, =CH).

66c: ^{1}H NMR (400 MHz): δ = 0.6 (s, 3H, Si-Me), 1.2–2.2 (m, 28H, 9-BBN), 6.7–7.2, 7.5 (m, m, 15H, Ph), 7.4 (s, 2H, =CH).

67c: ^{1}H NMR (C_6D_6): δ = 1.2–2.1 (m, 28H, 9-BBN), 6.8–7.3, 7.6, 8.2 (m, m, m, 22H, Si-Ph, Ph, =CH).

10.4.2.9. *Hydroboration of tetraalkyn-1-ylsilane derivatives **26b - d** with two equivalents of 9-BBN.*

A Schlenk tube was charged with tetrakis(*tert*-butylethynyl)silane **26b** (0.26 g, 0.74 mmol) and two equivalents of crystalline 9-BBN dimer (0.19 g, 1.48 mmol) were added. The reaction mixture was heated in toluene at 80 - 100 °C. The progress of the reaction was monitored by ^{29}Si NMR. After 20 min when twofold hydroboration was complete, all volatiles were removed under reduced pressure. The same procedure was adopted for the other members of the series, **26c** and **26d**. These compounds serve as starting materials for spirosilane (*vide infra*).

68b: ^{1}H NMR (400 MHz): δ = 1.3, 1.1 (s, s, 36H, ≡C-^{t}Bu, =C-^{t}Bu), 1.8 - 2.1 (m, 28H, 9-BBN), 6.7 (s, 2H, $^{3}J(^{1}H,^{29}Si)$ = 21.6 Hz, =CH).

68c: ^{1}H NMR (400 MHz): δ = 1.2 - 2.0 (m, 28H, 9-BBN), 7.4 (s, 2H, $^{3}J(^{1}H,^{29}Si)$ = 19.4 Hz, =CH), 6.6–7.2, 7.3 (m, m, 20H, Ph).

68d: ^{1}H NMR (400 MHz): δ = 1.4 - 2.3 (m, 28H, 9-BBN), 7.7 (s, 2H, $^{3}J(^{1}H,^{29}Si)$ = 19.7 Hz, =CH), 1.7, 2.1, 6.7, 7.0, 7.3, 7.6 (s, s, m, m, m, m, 28H, 4-Me-C_6H_4).

10.4.3. *Hydroboration of dialkyn-1-ylsilanes*

10.4.3.1. *Hydroboration of dialkyn-1-yl(chloro)silane **15** - **18** using BEt_3 and BPr_3.*

The mixture of the silane $Cl_2Si(C{\equiv}C\text{-}Bu)_2$ (0.28 g, 1.1 mmol) and BEt_3 (0.21 mL, 1.5 mmol, in slight excess) was sealed in an NMR tube and kept at 110 °C in an oil bath. After 24 d the reaction was found to be completed (^{29}Si NMR spectra). The NMR tube was cooled in liquid N_2 before opening, excess of BEt_3 and other volatiles were removed under reduced pressure and the product was obtained as a colorless oil, identified by NMR spectra as pure **72a**. The synthetic procedure for other compounds was similar to that of **72a** except of the reaction time, **69c** (5 d), **70c** (12 d), **71c** (15 d) and **73c** (6 d) .

69c: ^{1}H NMR not assigned due to the presence of some side products including siloles.

70c: ^{1}H NMR (400 MHz): δ = 0.7 (s, 3H, Si-Me), 0.9, 1.4 (t, m, 10H, BEt_2), 6.4 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 19.3 Hz, =CH), 6.9 - 7.4 (m, 10H, Ph, Ph).

71c: ^{1}H NMR (400 MHz): δ = 1.0, 1.5 (t, m, 10H, BEt_2), 6.5 (s, 1H, ^{3}J ($^{1}H,^{29}Si$) = 21.4 Hz, =CH), 6.8 - 7.4 (m, 15H, Si-Ph, Ph).

72a: ^{1}H NMR (400 MHz): δ = 0.9, 1.0, 1.2 - 2.1 (t, t, m, 18H, Bu), 1.0, 2.2 (t, m, 10H, BEt_2), 5.4 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.0 Hz, =CH). EI-MS: m/z (%) = 331 (6) [M^+], 260 (76), 254 (100), 211 (45), 69 (45), 41 (76).

73a: ^{1}H NMR (400 MHz): δ = 0.9, 1.3, 2.1 (m, m, t, 18H, Bu), 1.1, 1.4 (t, m, 14H, BPr_2), 5.4 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.0 Hz, =CH).

10.4.3.2. *1,1-vinylboration of alkenyl(alkyn-1-yl)silanes **51 - 54** and **57 - 60** to afford 1-silacyclobutene derivatives.*

The 1,2-hydroboration of silane **18** with 9-BBN affords mixture of silane **50a** and **54a**. The mixture was heated in toluene at 120 °C (oil bath temperature) for 4 d. The NMR spectra indicate the formation of 1-silacyclobutene **77a**, and the silane **50a** remains unchanged as a side product (^{1}H NMR data). The same procedure was

adopted for the syntheses of other 1-silacyclobutenes, **74 - 76** except that the heating period was different for each reaction, **74a** (8 h), **75**,**a**, **c** (5 d), **78c**, **79a** (21 h), **79c** (2 d) and **76c**, **80a**, **c**, **81c** (10 - 12 h).

74a: ^{1}H NMR (400 MHz): δ = 0.5, 1.0 - 1.3, 2.0, 2.4 (t, m, m, m, 18H, Bu), 1.3 - 1.9 (m, 14H, 9-BBN), 5.9 (t, 1H $^{3}J(^{1}H,^{1}H)$ = 7.1 Hz, =CH), 6.9 - 7.7 (m, 10H, $SiPh_2$).

75a: ^{1}H NMR (400 MHz): δ = 0.8 (s, 3H, Si-Me), 0.8, 1.3, 2.3 (t, m, m, 18H, Bu), 1.3, 1.8 - 1.9 (m, m, 14H, 9-BBN), 5.8 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 6.9 Hz, $^{3}J(^{1}H,^{29}Si)$ = 22.1 Hz, =CH).

75c: ^{1}H NMR (400 MHz): δ = 0.4 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 7.1 Hz, Si-Me), 1.2 - 2.1 (m, 14H, 9-BBN), 6.6 - 7.2 (m, 11H, Ph, =CH).

76c: ^{1}H NMR (400 MHz): δ = 1.4 - 2.0 (m, 14H, 9-BBN), 6.8 - 7.2, 7.4, 7.9 (m, m, m, 16H, Si-Ph, Ph, =CH).

77a: ^{1}H NMR (400 MHz): δ = 0.7, 0.8, 1.2 - 1.5, 2.2, 2.3 (t, t, m, m, t, 18H, Bu), 1.7 - 2.1 (m, 14H, 9-BBN), 5.8 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.0 Hz, =CH).

78c: ^{1}H NMR (400 MHz): δ = 1.1–1.9 (m, 14H, 9-BBN), 4.8 (s, 1H, $^{1}J(^{1}H,^{29}Si)$ = 196.9 Hz, Si-H), 6.0 (s, 1H, ^{3}J ($^{1}H,^{29}Si$) = 18.6 Hz, =CH), 6.7–7.6 (m, 15H, Si-Ph, Ph).

79a: ^{1}H NMR (400 MHz): δ = 0.4 (s, 3H, Si-Me), 0.9, 0.8 - 1.0, 1.7 (t, m, m, 9H, Bu), 1.0 - 1.9 (m, 14H, 9-BBN), 5.8 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.2 Hz, =CH), 6.6 - 7.4 (m, 10H, Si-Ph, Ph).

79c: ^{1}H NMR (400 MHz): δ = 0.2 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 6.6 Hz, Si-Me), 0.9 - 2.0 (m, 14H, 9-BBN), 6.7 - 7.4 (m, 15H, Si-Ph, Ph), 7.9 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 15.7 Hz, =CH).

80a: M. p. = 80 °C; ^{1}H NMR (400 MHz): δ = 0.7, 1.2–1.3, 2.3 (t, m, m, 9H, Bu), 1.4–2.0 (m, 14H, 9-BBN), 6.3 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.2 Hz, =CH), 7.1 - 7.9 (m,15H, $SiPh_2$, Ph).

80c: ^{1}H NMR (400 MHz): δ = 1.4–2.0 (m, 14H, 9-BBN), 7.4 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 19.6 Hz, =CH), 6.8 - 8.0 (m, 20H, $SiPh_2$, Ph).

81c: ^{1}H NMR (400 MHz): δ = 0.05 (s, 9H, $SiMe_3$), 0.44 (s, 3H, Si-Me), 1.07 - 1.98 (m, 14H, 9-BBN), 6.93 - 7.63 (m, 10H, 1H, SiPh, Ph, =CH).

10.4.3.3. *1,1-vinylboration of alkenyl(dialkyn-1-yl)silanes **62**, **63**, **65** and dialkenyl-(alkyn-1-yl)silanes **66** and **67**.*

The mixture containing silanes **62c** and **66c** was heated at 80 - 100 °C in an NMR tube for 2 - 4 h in C_6D_6. The reaction was monitored by ^{29}Si NMR spectroscopy to show the presence of **82c** and **85c**. They could be distinguished from their characteristic NMR data. The same experimental procedure was followed for the

formation of 1-silacyclobutene derivatives **83**, **84** and **86**. A slight variation in the reaction time was observed, rearrangement of silanes **65 - 67** took 24 h to afford heterocycles **84 - 86**.

82c: ^{1}H NMR (400 MHz): δ = 0.2 (s, 3H, Si-Me), 1.6 - 1.9 (m, 14H, 9-BBN), 6.7 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 14.6 Hz, =CH), 6.6 - 7.1 (m, 15H, Ph).

83c: ^{1}H NMR (400 MHz): δ = 1.4–2.1 (m, 14H, 9-BBN), 6.8–8.2 (m, 21H, SiPh, Ph, =CH).

83d: ^{1}H NMR (400 MHz): δ = 1.4 - 2.1 (m, 14H, 9-BBN), 1.8, 1.8, 6.5–8.2 (s, s, m, 27H, 4-Me-C_6H_4, Si-Ph, =CH).

84c: ^{1}H NMR (400 MHz): δ = 1.0, 1.1 (s, s, 18H, ^{t}Bu), 1.1, 1.4 (t, m, 10H, BEt_2), 6.3 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 18.6 Hz, =CH), 6.8–8.1 (m, 10H, Si-Ph, Ph).

85c: ^{1}H NMR (400 MHz): δ = 0.5 (s, 3H, Si-Me), 1.6 - 1.9 (m, 28H, 9-BBN), 6.6 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 13.4 Hz, =CH), 6.6 - 7.1, 7.4 (m, m, 15H, Ph), 7.8 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 15.6 Hz, =CH).

86c: ^{1}H NMR (400 MHz): δ = 1.4 - 2.1 (m, 28H, 9-BBN), 6.8 - 8.2 (m, 21H, Si-Ph, Ph, =CH), 8.3 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 17.6 Hz, =CH).

10.4.3.4. *Conversion of **68** into **88** via intramolecular 1,1-vinylboration*.

The silane **68b** (0.22 g, 0.37 mmol) was sealed in NMR tube and was heated at 80 - 100 °C for 3 - 4 h, using C_6D_6 as the solvent. During this time the intermediate **68b** was finally converted into the spirosilane **88b**. The same synthetic procedure was adopted for the conversion of **68c** and **68d**. They afforded selectively the corresponding spirosilanes **88c** and **88d**. The heating period for complete conversion of **68c** into **88c** and **68d** into **88d** was comparitively long (8 - 10 h).

88b: ^{1}H NMR (400 MHz): δ = 1.2, 1.2 (s, s, 36H, ^{t}Bu), 1.5, 2.2 (m, 28H, 9-BBN), 5.9 (s, 2H, $^{3}J(^{1}H,^{29}Si)$ =18.2 Hz, =CH).

88c: ^{1}H NMR (400 MHz): δ = 1.6 - 2.3 (m, 28H, 9-BBN), 7.5 (s, 2H, =CH), 6.9 - 7.8 (m, 20H, Ph); EI-MS: m/z (%) = 676 (1) [M^+], 555 (13) [M^+ - $C_8H_{13}B$], 436 (100) [M^+ - $C_{16}H_{26}B_2$], 359 (5) [M^+ - $C_{22}H_{31}B_2$].

88d: Yield after recrystallization from hexane = 39 %; m. p. = 230 °C; ^{1}H NMR (400 MHz): δ = 1.6 - 2.3 (m, 28H, 9-BBN), 1.9, 2.0, 6.8, 6.9, 7.3, 7.6 (s, s, m, m, m, m, 28H,4-Me-C_6H_4), 7.4 (s, 2H, $^{3}J(^{1}H,^{29}Si)$ = 17.3 Hz, =CH).

10.4.4. Hydroboration of alkyn-1-yl(vinyl)silanes

10.4.4.1. *Hydroboration of monoalkyn-1-yl(vinyl)silanes **8 - 10** using 9-BBN as hydroborating reagent*

A Schlenk tube was charged with a solution of **8a** (0.92 g, 4.96 mmol) in THF (10 mL). An equimolar amount of 9-BBN dimer (0.62 g) was added in one portion. The reaction mixture was stirred at room temperature, after 2 h all the volatiles were removed under reduced pressure and the oily residue was identified as 1-silacyclopent-2-ene **89a** based on its characteristic NMR data. The same experimental procedure was followed for the synthesis of 1-silacyclopent-2-enes **90** and **91** in the same series.

89a: ^{1}H NMR (400 MHz): δ = 0.5 (s, 3H, $^2J(^1H,^{29}Si)$ = 7.1 Hz, Si-Me), 0.9, 1.3, 1.5, 2.4 (t, m, m, m, 9H, Bu).1.3, 1.9 (m, 14H, 9-BBN), 0.8 (ddd, 1H, $^2J(^1H,^1H)$= 15.6 Hz, $^3J(^1H,^1H)$= 5.0 Hz, 9.2 Hz, C^5H_2), 1.1 (ddd, 1H, $^2J(^1H,^1H)$= 15.6 Hz, $^3J(^1H,^1H)$= 3.5 Hz, 9.0 Hz, C^5H_2), 2.5, 2.6 (m, m, 2H, C^4H_2); MS: m/z (%) = 308 [M^+] (85), 173 [M^+ - Cl] (5), 265 [M^+ - C_3H_7] (17), 251 [M^+ - Bu] (36), 188 [M^+ - C_8H_{13}] (17), 187 [M^+ - BBN] (12), 153 (100), 152 (63).

89b: ^{1}H NMR (400 MHz): δ = 0.6 (s, 3H, $^2J(^1H,^{29}Si)$ = 6.7 Hz, Si-Me), 1.1 (s, 9H, ^{t}Bu), 1.6 - 2.0 (m, 14H, 9-BBN), 0.8 (ddd, 1H, $^2J(^1H,^1H)$= 15.3 Hz, $^3J(^1H,^1H)$= 5.6 Hz, 8.8 Hz, C^5H_2), 1.0 (ddd, 1H, $^2J(^1H,^1H)$= 15.3 Hz, $^3J(^1H,^1H)$= 4.1 Hz, 8.4 Hz, C^5H_2), 2.4 (m, 2H, C^4H_2).

89c: M. p. = 51 - 52 °C; ^{1}H NMR (400 MHz): δ = -0.3 (s, 3H, Si-Me, $^2J(^1H,^{29}Si)$ = 7.4 Hz), 0.9 - 1.9 (m, 14H, 9-BBN), 0.8 (m, 2H, C^5H_2), 2.0 (m, 2H, C^4H_2), 6.4 - 7.0 (m, 5H, Ph); MS: m/z (%) 328 (53) [M^+], 293 (2) [M^+ - Cl], 207 (10) [M^+ - BBN], 172 (100).

90a: ^{1}H NMR (400 MHz): δ = 0.7, 1.4, 2.6 (t, m, m, 9H, Bu), 1.2, 1.8 (m, m, 14H, 9-BBN), 1.2 (m, 2H, C^5H_2), 2.4 (m, 2H, C^4H_2), 7.2, 7.7 (m, m, 5H, Si-Ph).

90c: M. p. = 43 - 45 °C; ^{1}H NMR (400 MHz): δ = 1.3 - 1.8 (m, 14H, 9-BBN), 0.8, 1.3 (m, m, 2H, C^5H_2), 2.8 (m, 2H, C^4H_2), 6.9 - 7.1, 7.6 (m, m, 10H, Si-Ph, Ph).

91a: ^{1}H NMR (400 MHz): δ = 0.8, 1.3, 2.4 (t, m, m, 9H, Bu), 1.2 - 1.9 (m, 14H, 9-BBN), 1.1 (m, 2H, C^5H_2), 2.4 (m, 2H, C^4H_2); MS: *m/z* (%) = 328 (44) [M^+], 286 (8) [M^+ - C_3H_7], 271 (32) [M^+ - C_4H_8], 244 (89), 208 (9) [M^+ - BBN], 122 (100), 110 (31).

91c: ^{1}H NMR (400 MHz): δ = 1.2 - 1.5 (m, 14H, 9-BBN), 1.1 (m, 2H, C^5H_2), 2.3 (m, 2H, C^4H_2), 6.6 - 7.0 (m, 5H, Ph); MS: *m/z* (%) = 349 (49), 348 (100) [M^+ - H], 313 (15) [M^+ - Cl], 239 (61), 228 (86) [M^+ - BBN], 192 (72).

10.4.4.2. *Hydroboration of **19** and **20** with one equivalent of 9-BBN, syntheses of **92** and **93**.*

The silane **19a** (0.57 g, 2.47 mmol) was dissolved in THF (10 mL) and one equivalent of 9-BBN (0.32 g, 2.47 mmol) was added in one portion. The reaction mixture was stirred at room temperature for 3 h. All volatiles were removed under reduced pressure and colorless oily liquid left was identified as **92a**. For the preparation of **92c** and **93a**, **c** the same method was followed.

92a: ^{1}H NMR (400 MHz): δ = 0.4 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 7.0 Hz, Si-Me), 0.8, 0.9, 1.3, 2.1 (t, t, m, t, 18H, Bu), 1.2 - 1.9 (m, 14H, 9-BBN), 0.8 (ddd, 1H, $^{2}J(^{1}H,^{1}H)$ = 14.9 Hz, $^{3}J(^{1}H,^{1}H)$ = 4.7 Hz, 9.0 Hz, $C^{5}H_{2}$), 1.2 (ddd, 1H, $^{2}J(^{1}H,^{1}H)$ = 14.9 Hz, $^{3}J(^{1}H,^{1}H)$ = 4.5 Hz, 9.2 Hz, $C^{5}H_{2}$), 2.5, 2.7 (m, m, 2H, $C^{4}H_{2}$).

92c: ^{1}H NMR (400 MHz): δ = 0.3 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 7.1 Hz, Si-Me), 1.2 - 1.6 (m, 14H, 9-BBN), 0.9 (ddd, 1H, $^{2}J(^{1}H,^{1}H)$ = 15.0 Hz, $^{3}J(^{1}H,^{1}H)$ = 5.4 Hz, 8.9 Hz, $C^{5}H_{2}$), 1.3 (m, 1H, $C^{5}H_{2}$), 2.7 (m, 2H, $C^{4}H_{2}$), 6.7 - 7.2 (m, 10H, Ph).

93a: ^{1}H NMR (400 MHz): δ = 0.7, 1.2, 2.0 (t, m, t, 9H, ≡-Bu), 0.7, 1.5, 2.7 (t, m, m, 9H, =C-Bu), 1.2 - 1.8 (m, 14H, 9-BBN), 1.0, 1.3 (m, m, 2H, $C^{5}H_{2}$), 2.4, 2.5 (m, m, 2H, $C^{4}H_{2}$), 7.2, 7.8 (m, m, 5H, Si-Ph).

93c: ^{1}H NMR (400 MHz): δ = 1.2 - 1.9 (m, 14H, 9-BBN), 1.2 (m, 2H, $C^{5}H_{2}$), 2.8 (m, 2H, $C^{4}H_{2}$), 6.8 - 7.8 (m, 15H, Si-Ph, Ph).

10.4.4.3. *Hydroboration of **92** and **93** with one equivalent of 9-BBN, syntheses of **94** and **95***

Equimolar amount of 9-BBN (0.32 g, 2.5 mmol) was added to 1-silacyclopent-2-ene derivative **92a** (2.5 mmol) in an NMR tube using C_6D_6 as the solvent. The reaction mixture was heated to 80 - 100 °C for 2 - 3 h. The product was identified as **94a**, based on NMR data. The same experimental procedure was adopted for the syntheses of **94c** and **95a**, **c**. All the compounds were obtained in almost quantitative yield (ca. 95 %; from NMR data).

94a: ^{1}H NMR (400 MHz): δ = 0.5 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 6.5 Hz, Si-Me), 0.9, 0.9, 1.4, 2.5 (t, t, m, m, 18H, Bu), 1.6 - 2.0 (m, 28H, 9-BBN), 0.9 (m, 1H, $C^{5}H_{2}$), 1.1 (ddd, 1H, $^{2}J(^{1}H,^{1}H)$ = 15.0 Hz, $^{3}J(^{1}H,^{1}H)$ = 5.5 Hz, 8.0 Hz, $C^{5}H_{2}$), 2.3, 2.8 (m, m, 2H, $C^{4}H_{2}$), 6.9 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.1 Hz, =CH).

94c: ^{1}H NMR (400 MHz): δ = 0.4 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 6.4 Hz, Si-Me), 1.5–2.1 (m, 28H, 9-BBN), 0.6 (ddd, 1H, $^{2}J(^{1}H,^{1}H)$ = 14.2 Hz, $^{3}J(^{1}H,^{1}H)$ = 5.5 Hz, 7.8 Hz, $C^{5}H_{2}$),

0.8 (ddd, 1H, $^{2}J(^{1}H,^{1}H)$ = 14.2 Hz, $^{3}J(^{1}H,^{1}H)$ = 5.8 Hz, 8.1 Hz, $C^{5}H_{2}$), 3.1 (m, 2H, $C^{4}H_{2}$), 6.5–6.9 (m, 10H, Ph), 7.6 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 16.1 Hz, =CH).

95a: ^{1}H NMR (400 MHz): δ = 0.7, 0.8, 1.3 - 1.4, 2.1, 2.5 (t, t, m, m, m, 18H, Bu), 1.3 - 1.9 (m, 28H, 9-BBN), 1.2 (m, 2H, $C^{5}H_{2}$), 2.8 (m, 2H, $C^{4}H_{2}$), 7.1 - 7.6 (m, 6H, Si-Ph, =CH).

95c: ^{1}H NMR (400 MHz): δ = 1.4–1.9 (m, 28H, 9-BBN), 1.3 (m, 2H, $C^{5}H_{2}$), 2.9 (m, 2H, $C^{4}H_{2}$), 7.0 - 7.2, 7.6, 7.6 (m, m, m, 15H, Si-Ph, Ph), 8.3 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 16.9 Hz, =CH).

10.4.4.4. *Hydroboration of dialkyn-1-yl(allyl)silane **21c** with one and two equivalents of of 9-BBN*

A Schlenk tube was charged with a solution of **21c** (1.35 g, 4.7 mmol) in THF and one equivalent of 9-BBN (0.59 g). The reaction mixture was stirred at room temperature for 2 - 3 h. All volatile materials were removed under reduced pressure and the oily product left was studied. The NMR data show **96c**, formed in high yield (ca. 98 %). The silane **96c** was dissolved in toluene (10 mL) and one further equivalent (0.59 g) of 9-BBN was added and the reaction mixture was heated to 100 °C. After 1 h, all volatiles were removed in a vacuum and the oily product left was identified as **97c** from its characteristic NMR data.

96c: ^{1}H NMR (400 MHz): δ = 0.3 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 6.9 Hz, Si-Me), 1.3 - 1.9 (m, 14H, 9-BBN), 0.9 (m, 2H, $C^{6}H_{2}$), 1.9 (m, 2H, $C^{5}H_{2}$), 2.4 (m, 2H, $C^{4}H_{2}$), 6.9 - 7.4 (m, 10H, Ph).

97c: ^{1}H NMR (400 MHz): δ = 0.3 (s, 3H, Si-Me), 1.4 - 2.1 (m, 28H, 9-BBN), 1.0 (m, 2H, $C^{6}H_{2}$), 2.0 (m, 2H, $C^{5}H_{2}$), 2.7 (m, 2H, $C^{4}H_{2}$), 7.1 - 7.3, 7.6 (m, m, 10H, Ph), 8.1 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 15.8 Hz, =CH).

10.4.4.5. *Syntheses of 1-silacyclopent-2-ene derivatives, **98a**, **99a** and 2,7-bis-[9-(9-borabicyclo[3.3.1]nonyl)]-1,6-[R,R´]-5-silaspiro[4.4]nona-1,6-dienes **100** and **101**.*

A Schlenk tube was charged with the solution of **22a** (1.60 g, 6.6 mmol) and one equivalent of 9-BBN (0.82 g, 6.6 mmol) in THF (10 mL). The reaction mixture was stirred at room temperature for 2 - 4 h, all volatile materials were removed under reduced pressure. A small part of the residue was dissolved in $C_{6}D_{6}$ and analysed by NMR spectroscopy. The reaction afforded a mixture of **22a** (starting silane), **98a** and

100a. A further equivalent of 9-BBN (0.82 g) was added using the same conditions and **100a** was obtained. The procedure for the preparation of spirosilane**100c**, **100e** and **101a** was exactly the same.

98a: ^{1}H NMR (400 MHz): δ = 2.1, 2.0, 1.5, 0.8, 0.7 (t, t, m, t, t, 18H, Bu), 6.0–6.2 (m, 3H, Si-vinyl), other signals were not assigned due to overlap with signals belonging to other compounds in the mixture.

99a: ^{1}H NMR (400 MHz): δ = 6.1, 6.3 (m, m, 3H, Si-vinyl), other signals were not assigned.

100a: ^{1}H NMR (400 MHz): δ = 0.9, 1.3, 2.4 (t, m, t, 18H, Bu), 1.3 - 1.9 (m, 28H, 9-BBN), 0.9, 1.0 (m, m, 4H, $C^{4,9}H_2$), 2.7 (m, 4H, $C^{3,8}H_2$).

100c: M. p. = 104 - 106 °C; Yield after recrystalization from pentane = 93 %; ^{1}H NMR (400 MHz): δ = 1.4 - 1.9 (m, 28H, 9-BBN), 1.1 (ddd, 1H, $^{2}J(^{1}H,^{1}H)$ = 15.5 Hz, $^{3}J(^{1}H,^{1}H)$ = 5.3, 9.3 Hz, $C^{4,9}H_2$), 1.2 (ddd, 1H, $^{2}J(^{1}H,^{1}H)$ = 15.5 Hz, $^{3}J(^{1}H,^{1}H)$ = 3.7, 9.1 Hz, $C^{4,9}H_2$), 2.8 (ddd, 1H, $^{2}J(^{1}H,^{1}H)$ = 18.2 Hz, $^{3}J(^{1}H,^{1}H)$ = 5.3, 9.3 Hz, $C^{3,8}H_2$), 2.9 (ddd, 1H, $^{2}J(^{1}H,^{1}H)$ = 18.2 Hz, $^{3}J(^{1}H,^{1}H)$ = 3.7, 9.1 Hz, $C^{3,8}H_2$), 7.0, 7.1, 7.2 (m, m, m, 10H, Ph).

100e: ^{1}H NMR (400 MHz): δ = 1.4 - 1.9 (m, 28H, 9-BBN), 1.1 (m, 4H, $C^{4,9}H_2$), 2.8 (m, 4H, $C^{3,8}H_2$), 1.2, 7.1, 7.2 (s, m, m, 26H, 4-^{t}Bu-C_6H_4).

101a: ^{1}H NMR (400 MHz): δ = 1.3 - 1.9 (m, 28H, 9-BBN), 0.8, 1.5, 2.7 (t, m, t, 9H, Bu), 1.3 (m, 4H, $C^{4,9}H_2$), 2.9 (m, 4H, $C^{3,8}H_2$), 1.2, 7.1, 7.2 (s, m, m, 13H, 4-^{t}Bu-C_6H_4).

10.4.5. *Syntheses of siloles*

10.4.5.1. *1,1-Ethylboration of silanes **11 - 17**, syntheses of siloles*.

General procedure: A Schlenk tube was charged with a solution of dialkyn-1-ylsilane and triethylborane in slight excess. The reaction solution was heated at 100 - 120 °C (oil bath temperature) for several days. The reaction was monitored by ^{29}Si NMR. After it was completed, all the volatiles were removed under reduced pressure and the brown oily residue was studied by NMR spectroscopy. Except for the reaction time, the experimental procedure was the same for all siloles. Time required for reaction completion was 2 d (**102c**, **102d**), 3 d (**103a**, **c**), 7 d (**107a**), 27 h at 140 °C (**104a**), 10 d (**104c**, **106c**), 23 d (**105a**), and 20 d (**108a**).

102c: ^{1}H NMR (400 MHz): δ = 0.2 (d, 3H, $^{3}J(^{1}H,^{1}H)$ = 4.2 Hz, Si-Me), 0.8, 1.4 (t, m, 10H, BEt_2), 1.0, 2.2 (t, m, 5H, Et), 5.0 (q, 1H, $^{3}J(^{1}H,^{1}H)$ = 4.2 Hz, $^{1}J(^{1}H,^{29}Si)$ = 190.9 Hz, Si-H), 6.9 - 7.1, 7.1 - 7.2 (m, m, 10H, Ph).

102d: ^{1}H NMR (400 MHz): δ = 0.3 (d, 3H, $^{2}J(^{1}H,^{1}H)$ = 4.2 Hz, Si-Me), 1.0, 1.4 (t, m,10H, BEt_2), 0.8, 2.2, 2.4 (t, m, m, 5H, Et), 5.1 (q, 1H, $^{1}J(^{1}H,^{29}Si)$ = 190.0 Hz, Si-H), 2.1, 2.1, 6.9, 7.2, 8.0 (s, s, m, m, m, 14H, 4-Me-C_4H_6).

103a: ^{1}H NMR (400 MHz): δ = 1.0, 1.1 - 1.4, 2.0 - 2.2 (t, m, m, 18H, Bu), 0.9, 1.3 (t, m, 10H, BEt_2), 0.7, 1.3 (t, m, 5H, Et), 5.2 (s, 1H, $^{1}J(^{1}H,^{29}Si)$ = 189.6 Hz, Si-H), 7.1 - 7.6 (m, 5H, Si-Ph).

103c: ^{1}H NMR (400 MHz): δ = 0.7, 1.2 (t, m, 10H, BEt_2), 0.9, 2.1 (t, m, 5H, Et), 5.5 (s, 1H, $^{1}J(^{1}H,^{29}Si)$ = 197.4 Hz, Si-H), 6.7 - 7.8 (m, 15H, Si-Ph, Ph).

104a: ^{1}H NMR (400 MHz): δ = 0.5 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 6.5 Hz, Si-Me), 0.5, 0.5, 1.0 - 0.9, 2.2 (t, t, m, m, 18H, Bu), 0.7, 1.8 - 1.9, (t, m, 10H, BEt_2), 0.6, 1.8 (t, m, 5H, Et), 6.9 - 7.4 (m, 5H, Si-Ph).

104c: ^{1}H NMR (400 MHz): δ = 0.6 (s, 3H, Si-Me), 1.1, 1.5 (t, m, 10H, BEt_2), 0.9, 2.4 (t, m, 5H, Et), 7.3 - 7.7 (m, 15H, Si-Ph, Ph).

105a: ^{1}H NMR (400 MHz): δ = 0.4, 0.5, 0.9, 1.3, 2.1 - 1.9 (t, t, m, m, m, 18H, Bu), 0.9, 1.1 (t, m, 10H, BEt_2), 0.8, 2.2 (t, m, 5H, Et), 6.9 - 7.7 (m, 10H, $SiPh_2$).

106c: ^{1}H NMR (400 MHz): δ = 1.1, 1.2 - 1.5 (t, m, 10H, BEt_2), 0.9, 2.1 (t, q, 5H, Et), 5.6 (s, 1H, $^{1}J(^{1}H,^{29}Si)$ = 234.9 Hz, Si-H), 6.8 - 7.0, 7.1 - 7.3 (m, m, 10H, Ph).

107a: ^{1}H NMR (400 MHz): δ = 0.5 (s, 3H, Si-Me), 0.9, 1.5 (t, m, 10H, BEt_2), 1.0, 2.3 (t, m, 5H, Et), 0.8, 0.8, 1.3, 2.2 (t, t, m, m, 18H, Bu).

108a: ^{1}H NMR (400 MHz): δ = 0.6 - 1.4, 1.8 - 2.5 (overlapping multiplets of Bu, BEt_2 and Et groups), 7.1, 7.7 (m, m, 5H, Si-Ph).

109c: Yield after recrystallization from pentane = 87 %; m. p. = 111 - 115 °C; ^{1}H NMR (400 MHz): δ = 0.8, 1.1, 1.4, 1.6, 1.9 - 2.0, 3.3 (t, q, m, m, m, t, 19H, 9-Et-9-BBN), 5.4 (br, 1H, $^{1}J(^{1}H,^{29}Si)$ = 197.5 Hz, Si-H), 6.7 - 7.0, 7.5 (m, m, 15H, Si-Ph, Ph).

10.4.5.2. *Synthesis of 1-alkenyl- and 1-alkyn-1-yl-substituted siloles **110 - 113***

The silanes **24** and **25** were mixed with BEt_3 (in excess), and the reactions were carried out at the same temperature as for siloles **102 - 108**. Silane **24** led to silole derivatives **112a** and **112c** quantitatively, while in case of silane **25** the major products were obtained as siloles **111a** and **111c**. The time required to induce

complete 1,1-ethylboration was different for different siloles, such as, 25 d (**111a**), 30 d (**111c**), 3 d (**112a**) and 10 d (**112c**).

111a: ^{1}H NMR (300 MHz): δ = 0.6, 1.0 - 1.4, 2.0 (t, m, m, 27H, Bu), 0.8, 1.0 - 1.4 (t, m, 10H, BEt_2), 0.9, 2.3 (t, m, 5H, Et), 7.1, 7.8 (m, m, 5H, Si-Ph).

111c: ^{1}H NMR (400 MHz): δ = 0.8, 1.4 (t, m, 10H, BEt_2), 1.0, 2.2 (t, q, 5H, Et), 6.7 - 7.4, 8.0 (m, m, 20H, Si-Ph, Ph).

112a: ^{1}H NMR (300 MHz): δ = 0.2 (s, 3H, Si-Me), 0.9, 1.1, 1.3 - 1.5, 2.0, 2.2, 2.3 (multiplets for Bu, Et and BEt_2).

112c: ^{1}H NMR (400 MHz): δ = 0.4 (s, 3H, Si-Me), 0.7, 1.4 (t, m, 10H, BEt_2), 0.8, 2.1 (t, m, 5H, Et), 6.7 - 7.4 (m, 15H, Ph).

10.4.5.3. *1,1-Ethylboration of silanes **19 - 21**.*

Pure **19a** (0.23 g: 0.99 mmol) was given into an NMR tube and BEt_3 was added in slight excess. The NMR tube was sealed and kept at elevated temperature (100 - 120 °C, oil bath temperature). After three days all volatiles were removed in a vacuum, the brown oily liquid left was identified as silole **114a**. A portion of silole **114a** was mixed with BEt_3 and kept at the same temperature in a sealed NMR tube. After 20 d the NMR tube was opened, all volatile materials were removed under reduced pressure and the oily liquid left was identified as silole **117a**. The reaction conditions for syntheses of siloles **114c** to afford **117c** was similar except that heating period lasted for 5 d and 23 d, respectively. Reactions in the case of silole derivatives **115a** and **116c** continued for 8 d and 6 d, respectively.

114a: ^{1}H NMR (300 MHz): δ = 0.3 (s, 3H, $^2J(^1H,^{29}Si)$ = 6.7 Hz, Si-Me), 0.7, 0.7, 1.3, 2.1 (t, t, m, m, 18H, Bu), 1.1, 1.3 (t, m, 10H, BEt_2), 0.9, 2.3 (t, m, 5H, Et), 6.0 (dd, 1H, $^2J(^1H,^1H)$ = 4.2 Hz, $^3J(^1H,^1H)$ = 20.3 Hz, $=CH_2$), 6.1 (dd, 1H, $^2J(^1H,^1H)$ = 3.9 Hz, $^3J(^1H,^1H)$ = 14.6 Hz, $=CH_2$), 6.5 (dd, 1H, $^3J(^1H,^1H)_{cis}$ = 14.6 Hz, $^3J(^1H,^1H)_{trans}$ = 19.9 Hz, Si-HC=).

114c: ^{1}H NMR (400 MHz): δ = 0.5 (s, 3H, Si-Me), 1.1, 1.5 (t, m, 10H, BEt_2), 0.9, 2.3, 2.4 (t, m, m, 5H, Et), 5.9 (dd, 1H, $^2J(^1H,^1H)$ = 3.6 Hz, $^3J(^1H,^1H)$ = 20.3 Hz, $=CH_2$), 6.1 (dd, 1H, $^2J(^1H,^1H)$ = 3.6 Hz, $^3J(^1H,^1H)$ = 14.4 Hz, $=CH_2$), 6.4 (dd, 1H, $^3J(^1H,^1H)_{cis}$ = 14.4 Hz, $^3J(^1H,^1H)_{trans}$ = 20.2 Hz, Si-CH), 7.2, 7.3 (m, m, 10H, Ph).

115a: ^{1}H NMR (300 MHz): δ = 0.7, 0.8, 1.2, 1.4, 2.1 (t, t, m, m, m, 18H, Bu), 1.1, 1.4 (t, br, 10H, BEt_2), 0.9, 2.3 (t, m, 5H, Et), 6.0 (dd, 1H, $^2J(^1H,^1H)$ = 3.8 Hz, $^3J(^1H,^1H)$ =

20.3 Hz, $=CH_2$), 6.1 (dd, 1H, $^2J(^1H,^1H)$ = 3.8 Hz, $^3J(^1H,^1H)$ = 14.8 Hz, $=CH_2$), 6.5 (dd, 1H, $^3J(^1H,^1H)_{cis}$ = 14.7 Hz, $^3J(^1H,^1H)_{trans}$ = 20.3 Hz, Si-CH), 7.2, 7.7 (m, m, 5H, Si-Ph).

116c: ^{1}H NMR (400 MHz): δ = 0.3 (s, 3H, Si-Me), 1.0, 1.3 (t, m, 10H, BEt_2), 0.8, 2.1, 2.2 (t, m, m, 5H, Et), 1.7, 4.8, 5.7 (d, m, m, 5H, All), 7.0 - 7.2 (m, 10H, Ph).

117a, **c**: Compounds are proposed on the basis of ^{13}C and ^{29}Si NMR data.

10.4.5.4. *Hydroborylation of vinyl group in silole **114a** and **114c** using 9-BBN, Synthesis of silole **118a** and **118c**.*

A Schlenk tube was charged with solution of silole **114a** (0.13 g, 0.39.mmol) in THF (5 mL) and one equivalent of 9-BBN (0.05 g) was added in one portion. The reaction mixture was stirred at room temperature. After 2 h solvent and all other volatiles were removed under reduced pressure leaving the silole **118a** as oily liquid. The same procedure was followed for the synthesis of **118c**.

118a: ^{1}H NMR (400 MHz): δ = 0.3 (s, 3H, Si-Me), 0.9, 2.1, 2.3 (t, m, m, 5H, Et), 0.9 - 1.0, 1.2 - 1.8 (m, m, Bu, $Si(CH_2)_2$, BEt_2, 9-BBN).

118c: ^{1}H NMR (400 MHz): δ = 0.4 (s, 3H, Si-Me), 0.8, 2.3 (t, m, 5H, Et), 1.0, 1.1 - 1.8 (m, m, Bu, $Si(CH_2)_2$, BEt_2, 9-BBN), 6.9 - 7.2 (m, 10H, Ph).

10.4.5.5. *Syntheses of silole derivatives of **119** and **120**.*

Reactions for the preparation of silole derivatives **119** and **120** were carried out under harsh reaction conditions as discussed for aforementioned siloles. All these compounds were obtained as viscous oil. They were characterized and used in further reactions without purification. Time taken by different reactions: **119a** (2 d), **119c** (4 d), **119e** (10 d) and **120a** (5 d).

119a: ^{1}H NMR (400 MHz): δ = 1.0, 1.4 (t, br, 10H, BEt_2), 0.8, 2.1 (t, q, 5H, Et), 0.9, 0.9, 1.4, 2.1, 2.3 (t, t, m, t, t, 18H, Bu), 5.9 (dd, 1H, $^2J(^1H,^1H)$ = 4.0 Hz, $^3J(^1H,^1H)$ = 20.1, $=CH_2$), 6.0 (dd, 1H, $^2J(^1H,^1H)$ = 4.0 Hz, $^3J(^1H,^1H)$ = 14.6, $=CH_2$), 6.3 (dd, 1H, $^3J(^1H,^1H)_{cis}$ = 14.6 Hz, $^3J(^1H,^1H)_{trans}$ = 20.2, HC=).

119c: ^{1}H NMR (400 MHz): δ = 1.1, 1.5 (t, br, 10H, BEt_2), 0.9, 2.3 (t, q, 5H, Et), 6.0 (dd, 1H, $^2J(^1H,^1H)$ = 3.7 Hz, $^3J(^1H,^1H)$ = 20.0 Hz, $=CH_2$), 6.0 (dd, 1H, $^2J(^1H,^1H)$ = 3.6 Hz, $^3J(^1H,^1H)$ = 14.8 Hz, $=CH_2$), 6.3 (dd, 1H, $^3J(^1H,^1H)_{cis}$ = 14.8 Hz, $^3J(^1H,^1H)_{trans}$ = 20.0 Hz, HC=), 7.1 - 7.2, 7.3, 7.3 (m, m, m, 10H, Ph).

119e: ^{1}H NMR (400 MHz): δ = 0.9, 1.3 (t, br, 10H, BEt_2), 0.7, 2.2 (t, q, 5H, Et), 6.2 (dd, 2H, HC=), 5.8 (m, 4H, $=CH_2$), 1.0, 1.1, 6.9, 7.1 (s, s, m, m, 26H, 4-^{t}Bu-C_6H_4).

120a: ^{1}H NMR (400 MHz): δ = 0.9, 1.2 - 1.4 (t, m, 10H, BEt_2), 0.8, 2.0 (t, m, 5H, Et), 0.8, 1.2 - 1.4, 2.3 (t, m, t, 9H, Bu), 5.9 (dd, 1H, $^{2}J(^{1}H,^{1}H)$ = 3.8 Hz, $^{3}J(^{1}H,^{1}H)$ = 14.8 Hz, $=CH_2$), 5.9 (dd, 1H, $^{2}J(^{1}H,^{1}H)$ = 3.8 Hz, $^{3}J(^{1}H,^{1}H)$ = 19.8 Hz, $=CH_2$), 6.2 (dd, 1H, $^{2}J(^{1}H,^{1}H)_{cis.}$ = 14.8 Hz, $^{3}J(^{1}H,^{1}H)_{trans.}$ = 19.8 Hz, $=CH_2$), 1.1, 6.9, 7.1 (s, m, m, 13H, 4-^{t}Bu-C_6H_4).

10.4.6. Reaction of novel boryl-substituted silanes

10.4.6.1. *Reaction of alkenylsilanes **35c** with 2-(N-trimethylsilylamino)pyridine.*

A Schlenk tube was charged with solution of *(Z)-9-[1-(chloromethylphenylsilyl)-2-phenyl-vinyl]-9-borabicyclo[3.3.1]nonane,* **35c** (1.34 g, 3.5 mmol) in toluene and 2-(N-trimethylsilylamino)pyridine (3.5 mmol). [170] The reaction mixture was heated at 100 °C for 3 - 4 h. All volatiles were removed under reduced pressure. The products were dissolved in pentane and kept at low temperature (-35 °C) for several days. The solid settled down was taken up into NMR tube and studied by NMR spectroscopy. Rest of the solid was dissolved in C_6D_6 and was kept at room temperature. Colorless crystals of suitable dimensions appeared after 4 - 6 days. A single crystal was selected and the structural data were determined by X-ray diffraction.

121. Yield after recrystallization from benzene = 32.8 %; m. p. = 168 - 171 °C; ^{1}H NMR (400 MHz): δ = 0.8 (s, 3H, Si-Me), 1.3 - 2.8 (m, 14H, 9-BBN), 3.5 (s, 1H, NH), 5.4, 5.9, 6.6, 8.0 (d, t, t, d, 4H, 2-NH-C_5H_4N), 6.7, 6.8, 6.9, (m, m, m, 10H, Ph, Si-Ph), 8.0 (s, 1H, $^{3}J(^{1}H, ^{29}Si)$ = 20.2 Hz, =CH).

10.4.6.2. *Hydrolysis and oxidation of (Z)-9-[1-(chlorodiphenylsilyl)-2-phenyl-vinyl]-9-borabicyclo[3.3.1]nonane **36c***

Compound **36c** (0.33 g, 0.72 mmol) was subjected to hydrolysis and oxidation in a Schlenk tube by allowing slow (months) exchange of argon against air. The first change observed after a few days, was the formation of a small amount of a crystalline material at the wall of the tube. The crystals were separated, identified (NMR [141]) as 9-hydroxy-9-borabicyclo[3.3.1]nonane **122** and some of the crystals were found suitable for X-ray analysis. The remaining oil, still consisting mainly of **122** (NMR analysis), was taken up in a mixture of hexane and benzene (3:1) and the solution was left for further hydrolysis and oxidation for a period of several months. After that, a substantial amount (ca. 45 % relative to the Si-content of **36c**) of another

crystalline material **123** had precipitated at the bottom of the Schlenk tube, was separated and single crystals could be selected for X-ray analysis.

123: M. p. = 247 - 250 °C; ^{1}H NMR (400 MHz): δ = 6.9 - 7.1 (m, $SiPh_2$).

10.4.6.3. *Reactions of alkenylsilanes **38** and **39** with bis(trimethylstannyl)ethyne and trimethyl(propyn-1-yl)stannane.Formation of borolenes (**124** - **130**), allenes (**131** - **134**) and butadienes (**135** - **140**).*

A solution of alkenylsilane **37c** (0.53 g, 1.62 mmol) was prepared in hexane (10 mL) and an equimolar amount of bis(trimethylstannyl)ethyne (0.57 g) was added slowly at room temperature. The reaction mixture was allowed to stay at the same temperature for 30 - 40 min. The solvent volume was reduced to ca. 5 mL and the solution was kept undisturbed, to get crystals suitable for X-ray analysis. After 2 - 3 h colorless crystals appeared, hexane soluble fractions were separated and few crystals were used for NMR measurements. All other borolenes were prepared exactly in the same way and were studied by NMR spectroscopy, elemental analysis (**124c** and **126c**), mass spectrometry (**125c**, **128c**) as well as X-ray crystallography (**124c**, **126c**). In the case of **38a** and **39a** the reactions afford almost quantitatively allenes (**131a**; ca. 95 % and **132a**; ca. 50 %). The reactions of trimethyl(propyn-1-yl)stannane with the same silanes (**38a** and **39c**) afford complex mixtures containing borolene, allene and butadiene derivatives. The complete NMR assignments were not possible for such mixtures.

124c: M.p. = 133 - 135 °C; Crystals obtained in hexane = 72 %; ^{1}H NMR (400 MHz): δ = -0.1 (s, 9H, $^{2}J(^{1}H,^{119}Sn)$ = 54.0 Hz, $SnMe_3$), 0.2 (s, 9H, $^{2}J(^{1}H,^{119}Sn)$ = 52.6 Hz, $SnMe_3$), 1.2 - 1.9, 2.2, 2.9 (m, m, m, 14H, 9-BBN), 4.2 (s, 1H, $^{3}J(^{1}H,^{119}Sn)$ = 28.6, 6.9 Hz, $C^{4}H$), 5.2 (s, 1H, $^{1}J(^{1}H,^{29}Si)$ = 286.1 Hz, $^{3}J(^{1}H,^{119}Sn)$ = 7.8 Hz, Si-H), 6.9 - 7.1 (m, 5H, Ph); elemental analysis Calcd. (%): C 42.72, H 5.83; found (%): C 43.34, H 5.461.

125a: ca. 5 %, ^{1}H NMR signals were not assigned.

125c: ^{1}H NMR (400 MHz): δ = 0.01 (s, 9H, $^{2}J(^{1}H,^{119}Sn)$ = 54.5 Hz, $SnMe_3$), 0.3 (s, 9H, $^{2}J(^{1}H,^{119}Sn)$ = 52.6 Hz, $SnMe_3$), 0.2 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 7.8 Hz, Si-Me), 4.3 (s, 1H, $^{3}J(^{1}H,^{119}Sn)$ = 30.2, 7.1 Hz, $C^{4}H$), 3.0, 2.5, 1.3 - 2.1, 2.5, 3.0, (m, m, m, 14H, 9-BBN), 6.9 - 7.3 (m, 5H, Ph); EI-MS: m/z (%) = 688 (5) [M^+], 673 (100) [M^+ - CH_3], 674 (81) [M^+ - CH_4], 653 (4) [M^+ - Cl], 510 (51) [M^+ - $SnMe_3$], 489 (5) [M^+ - $Sn(Cl)Me_3$], 289 (28), 165 (79).

126a: ^{1}H NMR (400 MHz): δ = 0.1 (s, 9H, $^{2}J(^{1}H,^{119}Sn)$ = 54.2 Hz, $SnMe_3$), 0.1 (s, 9H $^{2}J(^{1}H,^{119}Sn)$ = 55.0 Hz, $SnMe_3$), 0.9, 1.2 - 1.3, 2.5 (t, m, m, 9H, Bu), 1.6 - 1.9, 2.4, 2.8 (m, m, m, 14H, 9-BBN), 3.4 (t, 1H, $^{3}J(^{1}H,^{119}Sn)$ = 27.7 Hz, $^{3}J(^{1}H,^{1}H)$ = 4.6 Hz, $C^{4}H$), 7.0 - 7.8 (m, 5H, Si-Ph).

126c: M.p. = 144 - 145 °C; Crystals obtained in pentane = 83.8 %; ^{1}H NMR (400 MHz): δ = -0.1 (s, 9H, $^{2}J(^{1}H,^{119}Sn)$ = 54.6 Hz, $SnMe_3$), 0.3 (s, 9H, $^{2}J(^{1}H,^{119}Sn)$ = 52.3 Hz, $SnMe_3$), 1.3 - 1.9, 2.6, 2.9 (m, m, m, 14H, 9-BBN), 4.3 (s, 1H, $^{3}J(^{1}H,^{119}Sn)$ = 28.4, 7.2 Hz, $C^{4}H$), 6.6 - 7.3 (m, 10H, Si-Ph, Ph); elemental analysis Calcd. (%): C 47.99, H 5.77; found: C 48.32, H 5.77.

127c: ^{1}H NMR (400 MHz): δ = -0.1 (s, 9H $^{2}J(^{1}H,^{119}Sn)$ = 54.3 Hz, $SnMe_3$), 0.3 (s, 9H, $^{2}J(^{1}H,^{119}Sn)$ = 52.2 Hz, $SnMe_3$), 1.0, 1.2, 1.6, 1.9, 2.4, 2.5 (t, t, m, m, m, m, 10H, Et, BEt), 4.3 (s, 1H, $^{3}J(^{1}H,^{119}Sn)$ = 30.3, 8.2 Hz, $C^{4}H$), 6.7 - 7.8 (m, 10H, Ph, Si-Ph).

128a: ^{1}H NMR (400 MHz): δ = 0.2 (s, 9H, $^{2}J(^{1}H,^{119}Sn)$ = 53.5 Hz, $SnMe_3$), 0.2 (s, 9H, $^{2}J(^{1}H,^{119}Sn)$ = 52.8 Hz, $SnMe_3$), 0.8, 1.1 - 1.9, 2.1 (t, m, m, 9H, Bu), 3.3 (t, 1H, $^{3}J(^{1}H,^{119}Sn)$ = 26.8 Hz, $^{3}J(^{1}H,^{1}H)$ = 4.9 Hz, $C^{4}H$), 1.1 - 1.9, 2.4, 2.8 (m, m, m, 14H, 9-BBN).

128c: ^{1}H NMR (400 MHz): δ = -0.3 (s, 9H, $^{3}J(^{1}H,^{119}Sn)$ = 53.5 Hz, $SnMe_3$), 0.1 (s, 9H, $^{2}J(^{1}H,^{119}Sn)$ = 51.8 Hz, $SnMe_3$), 1.0 - 1.7, 2.2, 2.7 (m, m, m, 14H, 9-BBN), 4.2 (s, 1H, $^{3}J(^{1}H,^{119}Sn)$ = 28.6, 6.9 Hz, $C^{4}H$), 6.7 - 6.9 (m, 5H, Ph); EI-MS: m/z (%) = 690 (28) [M^{+}], 655 (10) [M^{+} - Cl], 526 (13) [M^{+} - C_3H_8Sn], 497 (10)[M^{+} - $C_4H_9Cl_3Si$], 165 (100).

129a: ^{1}H NMR (400 MHz): δ = 5.8 (t, 1H, $^{3}J(^{1}H,^{119}Sn)$ = 21.3 Hz, $^{1}J(^{1}H,^{1}H)$ = 7.8 Hz, $C^{4}H$) other protons were not assigned.

130c: ^{1}H NMR (400 MHz): δ = 4.5 (s, 1H, $^{3}J(^{1}H,^{119}Sn)$ = 21.9 Hz, $C^{4}H$).

131a: ^{1}H NMR (400 MHz): δ = 0.2 (s, 9H, $SnMe_3$), 0.2 (s, 9H, $SnMe_3$), 0.7 (s, 3H, Si-Me), 0.9, 1.1, 1.4, 1.8 - 2.1 (t, m, m, m, 9-BBN, Bu, -CH).

132a: ^{1}H NMR (400 MHz): δ = 0.2, 0.2 (s, s, 18H, $^{2}J(^{1}H,^{119}Sn)$ = 52.8 Hz, $SnMe_3$), other ^{1}H signals were overlapp multiplets with signals belonging to other compound **126a** (borolene) in the mixtures.

133a, **134c**, **135a** and **136c** were obtained as mixtures and their full and precise assignment was not possible.

10.4.6.4. *Protodeborylation of **88d** using acetic acid as protic reagent. Synthesis of 3,7-bis-(4-methylbenzylidene)-1,5-di(p-tolyl)-4-silaspiro[3.3]hepta-1,5-diene, **88d - P.***

To a solution of **88d** (in 5mL pentane) glacial acetic acid was added in slight excess. The reaction mixture was stirred at room temperature for 1 h, the boron-oxygen compound [161] was separated at low temperature as a solid, and volatile materials were removed under reduced pressure. The spiro-compound **88d - P** was obtained as colorless waxy solid.

88d - P: ^{1}H NMR (400 MHz): δ = 1.9, 1.8, 6.7, 6.8, 7.3, 7.4 (s, s, m, m, m, m, 28H, 4-Me-C_6H_4), 7.1 (s, 2H, $^{3}J(^{1}H,^{29}Si)$ = 17.3 Hz, =CH), 8.1 (s, 2H, $^{3}J(^{1}H,^{29}Si)$ = 22.3 Hz, $C^{3}H$).

10.4.6.5. *Synthesis of boron-oxygen compound, 1,5-dicyclooctyl-3,7-dimethyl-4,8,9-trioxa-2,6-dioxonia-1,5-diboratabicyclo[3.3.1]nona-2,6-diene **142**.*

Procedure1: To the solution of the respective silane **88** - **91** (1.7 mmol) in 5 mL of hexane, acetic acid (0.5 mL, in 5 fold excess), was added slowly at room temperature. After 30 - 40 min all volatile materials were removed in a vacuum. The oily mixture containing the protodeborylated silanes and boron-oxygen compound **142**, was taken up in pentane and kept at -25 °C for 24h. Solid materials settled down, were separated from the liquid fraction, dissolved in pentane, and kept at room temperature for crystallization. After a few days, crystals of **142**, suitable for X-ray structural analysis were obtained.

Procedure2: A Schlenk tube was charged with 9-borabicyclo[3.3.1]nonane dimer (1.14 g, 4.55 mmol) and hexane (10 mL). Acetic Acid (0.52 mL, 9 mmol) was added slowly at room temperature, and the reaction mixture was kept stirring for 12 h. All volatile materials were removed in a vacuum, and the solid residue was identified as 9-acetoxy-9-borabicyclo[3.3.1]nonane **141**, which was soluble in THF and much less soluble in pentane, hexane and benzene. The 9-acetoxy-9-borabicyclo[3.3.1]nonane **141** was taken up in benzene to give a suspension, and acetic acid was added in excess. The mixture was kept stirring for 40 minutes at room temperature and then, volatile materials were removed in a vacuum. The solid residue was dissolved in C_6D_6 and identified as pure **142** by its NMR data.

141: ^{1}H NMR (400 MHz): δ = 0.7 - 1.6, 1.8 (m, s, 9-BBN, CH_3).

142: Yield after recrystallization from hexane = 78 %; m. p. = 72 - 73 °C; ^{1}H NMR (400 MHz): δ = 1.3 (s, 3H, CH_3), 1.0, 1.6, 1.8, 2.0 (m, m, m, m, 15H, cyclooctyl).

10.4.6.6. *Protodeborylation of 1-silacyclopent-2-enes **89 - 91**.*

The same experimental procedure was adopted for the protdeborylation of 1-silacyclopent-2-enes (**89 - 91**) **- P** as for **88d - P**. The oily desired compounds (> 95 %, NMR data) were separated. The fractional distillation of oily liquids, mainly the desired silane was possible and they were obtained in high purity (99.9 %, Figure 7.11). Compound **90c - P** was dissolved in 2 mL of pentane, and after few days crystals suitable for single X-ray crystal analysis were obtained at room temperature.

89a - P: B. p. = 68 - 70 °C/1.28x10^{-1} Torr; ^{1}H NMR (400 MHz): δ = 0.4 (s, 3H, Si-Me), 0.8, 1.3, 1.9 (t, m, m, 9H, Bu), 0.9, 2.1 (m, m, 4H, C^5H_2, C^4H_2), 6.2 (m, 1H, C^3H).

89c - P: ^{1}H NMR (400 MHz) data: δ = 0.4 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 7.1 Hz, Si-Me), 0.7, (ddd, 1H, $^{2}J(^{1}H,^{1}H)$ = 15.8 Hz, , $^{3}J(^{1}H,^{1}H)$ = 4.9 Hz, 9.5 Hz, C^5H_2), 1.0 (ddd, 1H, $^{2}J(^{1}H,^{1}H)$ = 15.8 Hz, $^{3}J(^{1}H,^{1}H)_{cis}$ = 3.1 Hz, 9.2 Hz, C^5H_2), 2.3 (m, 1H, C^4H_2), 2.3 (m, 1H, C^4H_2), 6.7 (m, 1H, $^{3}J(^{1}H,^{1}H)$ = 3.1 Hz, $^{3}J(^{1}H,^{29}Si)$ = 17.2 Hz, C^3H), 7.0 - 7.4 (m, 5H, Ph).

90a - P: B. p. = 84 - 89 °C/1.8x10^{-2} Torr; yield = 89 %; ^{1}H NMR (400 MHz): δ = 0.7, 1.1, 1.3, 2.2 (t, m, m, t, 9H, Bu), 1.0, 2.3, (m, m, 2H, 2H, C^5H_2, C^4H_2), 6.4 (m, 1H, C^3H), 7.1, 7.6 (m, m, 5H, Si-Ph).

90c - P: b. p. = 130 - 135 °C/2.03x10^{-2} Torr; m. p. = 42 °C; Yield after recrystallization = 52 %; ^{1}H NMR (400 MHz): δ = 1.1 (ddd, 1H, $^{2}J(^{1}H,^{1}H)$ = 15.7 Hz, $^{3}J(^{1}H,^{1}H)$ = 4.7 Hz, 9.1 Hz, C^5H_2), 1.3 (ddd, 1H, $^{2}J(^{1}H,^{1}H)$ = 16.1 Hz, $^{3}J(^{1}H,^{1}H)_{cis}$ = 3.9 Hz, 9.1 Hz, C^5H_2), 2.4 - 2.5 (m, 2H, C^4H_2), 6.9 - 7.1, 7.4, 7.6 (m, m, m, 11H, Si-Ph, Ph, C^3H).

91a - P: ^{1}H NMR (400 MHz): δ = 0.8, 1.2, 2.2 (t, m, t, 9H, Bu), 1.0, 2.4 (m, m, 4H, C^5H_2, C^4H_2), 6.3 (s, 1H, C^3H).

10.4.6.7. *Protodeborylation of 1-silacyclopent-2-ene derivatives **92 - 95** and 1-silacyclohex-2-ene derivatives **96c** and **97c**.*

A known amount of **92a** (0.38 g, 1.07 mmol) was treated with excess of acetic acid in pentane. The reaction proceeded in the same way as for simple 1-silacyclopent-2-ene derivatives **89** - **91**. The desired silanes and oxygen-boron compound **142** was heated at 80 - 100 °C under reduced pressure for 1 - 2 hours, the compound **142** sublimed and accumulated along the walls of the schlenk tube as

colorless crystals, leaving **92a - P** as oily liquid in pure form (> 95 % from NMR data). All other reactions were performed exactly in the same way.

92a - P: ^{1}H NMR (300 MHz): δ = 0.3 (s, 3H, $^{2}J(^{1}H,^{1}H)$ = 7.3 Hz, Si-Me), 0.7, 0.9, 1.3, 2.1, 2.3 (t, t, m, t, m, 18H, C^{2}Bu, ≡C-Bu), 1.0 (ddd, 1H, $^{2}J(^{1}H,^{1}H)$ = 15.1 Hz, $^{3}J(^{1}H,^{1}H)$ = 4.7, 9.0 Hz, $C^{5}H_{2}$), 1.3 (m, 1H, $C^{5}H$), 2.3 (m, 2H, $C^{4}H_{2}$), 6.3 (m, 1H, $^{3}J(^{1}H,^{29}Si)$ = 14.6 Hz, $C^{3}H$).

92c - P: ^{1}H NMR (400 MHz): δ = 0.6 (s, 3H, Si-Me), 0.8 (ddd, 1H, $^{2}J(^{1}H,^{1}H)$ = 15.3 Hz, $^{3}J(^{1}H,^{1}H)$ = 4.7 Hz, 9.4 Hz, $C^{5}H_{2}$), 1.3 (ddd, 1H, $^{2}J(^{1}H,^{1}H)$ = 15.3 Hz, $^{3}J(^{1}H,^{1}H)_{cis}$. = 4.7 Hz, 9.4 Hz, $C^{5}H_{2}$), 2.4, 2.5 (m, m, 2H, $C^{4}H_{2}$), 6.8 (t, 1H, $C^{3}H$), 6.9, 7.2, 7.3, 7.7 (m, m, m, m, 10H, C^{2}Ph, ≡C-Ph).

93a - P: ^{1}H NMR (400 MHz): δ = 0.7, 0.8, 1.2, 2.1, 2.3 (t, t, m, t, m, 18H, C^{2}Bu, ≡C-Bu), 1.0 (m, 1H, $C^{5}H$), 1.2 (m, 1H, $C^{5}H_{2}$), 2.4 (m, 2H, $C^{4}H_{2}$), 6.4 (m, 1H, $^{3}J(^{1}H,^{29}Si)$ = 15.9 Hz, $C^{3}H$), 7.2, 7.7 (m, m, 5H, Si-Ph).

93c - P: ^{1}H NMR (400 MHz): δ =1.1, 1.3 (m, m, 2H, $C^{5}H_{2}$), 2.5 (m, 2H, $C^{4}H_{2}$), 7.0 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 3.0 Hz, $C^{3}H$), 6.9, 7.1, 7.2, 7.4, 7.6, 7.9 (m, m, m, m, m, 15H, Ph, Si-Ph).

94a - P: ^{1}H NMR (400 MHz): δ = 0.3 (s, 3H, Si-Me), 0.8, 0.9, 1.3, 2.1 (t, t, m, m, 18H, Bu), 1.0 (m, 2H, $C^{5}H_{2}$), 2.4 (m, 2H, $C^{4}H_{2}$), 5.6 (d, 1H, $^{3}J(^{1}H,^{1}H)$ = 13.9 Hz, =CH), 6.3 (s, 1H, $C^{3}H$), 6.3 (dt, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.3 Hz, 13.8 Hz, H(Bu)C=).

94c - P: ^{1}H NMR (300 MHz): δ = 0.3 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 6.5 Hz, Si-Me), 0.8 - 0.9 (m, 2H, $C^{5}H_{2}$), 2.4 (m, 2H, $C^{4}H_{2}$), 6.8 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 3.1 Hz, $^{3}J(^{1}H,^{29}Si)$ = 13.7 Hz, $C^{3}H$), 6.1 (d, 1H, $^{3}J(^{1}H,^{1}H)$ = 15.1 Hz, =CH), 7.4 (d, 1H, $^{2}J(^{1}H,^{1}H)$ = 15.1 Hz, =CH), 7.0–7.3, 7.4 (m, m, 10H, Ph).

95a - P: ^{1}H NMR (300 MHz): δ = 0.7, 0.7, 1.0 - 1.3, 2.0, 2.2 (t, t, m, m, t, 18H, Bu), 0.9 (m, 2H, $C^{5}H_{2}$), 2.5 (m, 2H, $C^{4}H_{2}$), 5.9 (d, 1H, $^{3}J(^{1}H,^{1}H)$ = 14.0 Hz, =CH), 6.4 (m, 1H, $C^{3}H$), 6.5 (dt, 1H, $^{3}J(^{1}H,^{1}H)$ = 7.3 Hz, $^{3}J(^{1}H,^{1}H)$ = 13.8 Hz, =C(Bu)H), 7.1, 7.2, 7.5 (m, m, 5H, Si-Ph).

95c - P: ^{1}H NMR (300 MHz): δ = 1.0 (m, 2H, $C^{5}H_{2}$), 2.4 (m, 2H, $C^{4}H_{2}$), 6.3 (d, 1H, $^{3}J(^{1}H,^{1}H)$ = 15.4 Hz, =CH), 6.9 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 3.2 Hz, $C^{3}H$), 7.5 (d, 1H, $^{3}J(^{1}H,^{1}H)$ = 15.4 Hz, =CH), 7.0 - 7.2, 7.3, 7.4, 7.7 (m, m, m, m, 15H, Si-Ph, Ph).

96c - P: ^{1}H NMR (400 MHz): δ = 0.5 (s, 3H, Si-Me), 0.9, 1.4, 2.3 (m, m, m, 6H, $C^{6}H_{2}$, $C^{5}H_{2}$, $C^{4}H_{2}$), 6.9 (t, 1H, $^{3}J(^{1}H,^{1}H)$ = 4.1 Hz, $C^{3}H$), 7.3, 7.4, 7.6, 7.8 (m, m, m, m, 10H, Ph).

97c - P: ^{1}H NMR (400 MHz): δ = 0.1 (s, 3H, Si-Me), 0.6, 0.7, 2.1 (m, m, m, $C^{6}H_2$, $C^{5}H_2$, $C^{4}H_2$), 5.9 (d, 1H, $^{3}J(^{1}H, ^{1}H)$ = 15.0 Hz, =CH), 6.6 (t, 1H, $^{3}J(^{1}H, ^{1}H)$ = 4.4 Hz, $C^{3}H$), 6.9 - 7.3 (m, 11H, Ph, H(Ph)C=).

10.4.6.8. *Protodeborylation of spirosilanes **100** and **101**, Syntheses of 1,6-dialkyl-5-silaspiro[4.4]nona-1,6-diene derivatives.*

Pure **100a** was mixed with acetic acid and the reaction was performed under the same conditions as discussed for above mentioned silanes.

100a - P: ^{1}H NMR (400 MHz): δ = 0.9, 1.6, 2.2 (t, m, t, 18H, Bu), 1.0 (m, 4H, $C^{4,9}H_2$), 2.4 (m, 4H, $C^{3,8}H_2$), 6.4 (m, 2H, $C^{2,7}H$).

100c - P: M. p. = 51 - 52 °C; Yield after recrystalization from hexane = 63 %; ^{1}H NMR (400 MHz): δ = 0.8 (ddd, 2H, $^{2}J(^{1}H,^{1}H)$ = 15.7 Hz, $^{3}J(^{1}H,^{1}H)$ = 4.4 Hz, 9.5 Hz, $C^{4,9}H_2$), 1.1 (m, 2H, $^{2}J(^{1}H,^{1}H)$ = 15.7 Hz, $^{3}J(^{1}H,^{1}H)$ = 4.1 Hz, 9.4 Hz, $C^{4,9}H_2$), 2.5 (m, 2H, $^{2}J(^{1}H,^{1}H)$ = 19.0 Hz, $C^{3,8}H_2$), 6.9, 7.4 (m, m, 10H, Ph), 7.1 (m, 2H, $C^{2,7}H$); GC/MS: t_R = 22.0 min, *m/z* (%) = 288.06 (41) [M^+], 134.3 (21) [$M^+ - C_{12}H_{10}$], 132.2 (72) [$M^+ - C_{12}H_{12}$], 158.0 (90) [$M^+ - C_{10}H_{10}$], 105.0 (100) [$M^+ - C_{12}H_{14}Si$].

100e - P: M. p. = 64 - 65 °C; Yield recovered after recrystalization form pentane = 20 %; ^{1}H NMR (400 MHz): δ = 0.9, 1.2 (m, m, 4H, $C^{4,9}H_2$), 2.5–2.6 (m, 4H, $C^{3,8}H_2$), 7.1 (t, 2H, $^{3}J(^{1}H,^{1}H)$ = 3.1 Hz, $^{3}J(^{1}H,^{29}Si)$ = 13.9 Hz, $C^{2,7}H$), 1.2, 7.2, 7.5 (s, m, m, 26H, 4-^{t}Bu-C_6H_4).

101a - P: ^{1}H NMR (400 MHz): δ = 0.8, 1.4, 2.3 (t, m, t, 9H, Bu), 0.9 (m, 4H, $C^{4,9}H_2$), 2.5 (m, 4H, $C^{3,8}H_2$), 7.0 (t, 1H, $C^{2}H$), 6.5 (m, 1H, $C^{7}H$), 1.2, 7.2, 7.4 (s, m, m, 13H, 4-^{t}Bu-C_6H_4); GC/MS: t_R = 26.2 min, *m/z* (%) = 400.11 (20) [M^+], 384.20 (13) [$M^+ - CH_3$], 343.20 (42) [$M^+ - C_4H_9$], 287.01 (8) [$M^+ - C_8H_{18}$], 56.99 (100) $[Si(CH_2)_2]^+$ or $[C_4H_8]^+$.

10.4.6.9. *Protodeborylation of siloles **102 - 104***

General procedure: To a solution of the respective silole in pentane (10 mL), an excess of acetic acid (2 - 3 fold) was added slowly and the reaction mixture was stirred at room temperature for 40 minutes. All volatiles were removed and the oily residue was identified as protodeborylated silole, accompanied by the boron-oxygen compound **143.** The same reaction was repeated for protodeborylation of all siloles observing identical experimental conditions. All siloles synthesized during the course of this dissertation were yellow or brown oily liquids.

102a - P: ^{1}H NMR (400 MHz): δ = 0.5 (s, 3H, Si-Me), 1.2, 2.1 (t, q, 5H, Et), 1.7 (s, 3H, Me), 0.9, 0.9, 1.3 - 1.5, 2.2 - 2.4 (t, t, m, m, 18H, Bu), 6.4 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 17.1 Hz, $C^{4}H$).

102c - P: ^{1}H NMR (400 MHz): δ = 0.5 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 7.0 Hz, Si-Me), 1.2, 2.2 (t, q, 5H, Et), 1.5 (s, 3H, Me), 7.1 (s, 1H, $C^{4}H$), 7.0, 7.2, 7.3, 7.5 (m, m, m, m, 10H, Ph).

102d - P: ^{1}H NMR (400 MHz): δ = 0.6 (s, 3H, Si-Me), 1.0, 2.3 (t, q, 5H, Et), 1.6 (s, 3H, Me), 7.1 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 15.6 Hz, $C^{4}H$), 2.1, 2.1, 7.0, 7.2, 7.5 (s, s, m, m, m, 14H, 4-Me-C_6H_4).

103a - P: ^{1}H NMR (400 MHz): δ = 0.8, 0.9, 1.3, 2.2 - 2.3 (t, t, m, m, 18H, Bu), 1.4 (s, 3H, Me), 1.1, 2.1 (t, q, 5H, Et), 7.2 (s, 1H, $C^{4}H$), 7.6 - 7.8 (m, 5H, Si-Ph).

103c - P: ^{1}H NMR (400 MHz): δ = 1.0, 2.3 (t, q, 5H, Et), 1.5 (s, 3H, Me), 6.9, 7.1, 7.2, 7.5, 7.8 (m, m, m, m, m, 15H, Si-Ph, Ph), 7.2 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 16.0 Hz, $C^{4}H$).

104a - P: ^{1}H NMR (400 MHz): δ = 0.5 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 6.5 Hz, Si-Me), 1.1, 2.2 (t, q, 5H, Et), 0.7, 0.8, 1.1, 1.3, 2.3 (t, t, m, m, t, 18H, Bu), 6.5 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 13.4 Hz, $C^{4}H$), 7.5, 7.1 (m, m, 5H, Si-Ph).

104c - P: ^{1}H NMR (400 MHz): δ = 0.6 (s, 3H, $^{2}J(^{1}H,^{29}Si)$ = 6.6 Hz, Si-Me), 1.0, 2.4 (t, q, 5H, Et), 7.3 (s, 1H, $^{3}J(^{1}H,^{29}Si)$ = 13.1 Hz, $C^{4}H$), 6.9 - 7.1, 7.4, 7.6, 7.9 (m, m, m, m, 15H, Si-Ph, Ph).

10.4.6.10. *Reaction of silole derivative **112a** with MeOH*

A solution of silole **112a** in hexane was given into a Schlenk tube and MeOH was added in excess. The reaction mixture was stirred for 1 - 2 h at room temperature. All volatile materials were evaporated. A part of the oily residue was dissoled in $CDCl_3$ and NMR spectra were measured. The data indicate the presence of the oxasilaboratole derivative **112a - P**.

112a - P: ^{1}H NMR (400 MHz): δ = 0.1 (s, 3H, Si-Me), 0.4 - 0.6, 0.9, 1.3, 2.1, (m, m, m, m, all protons of Bu, Et and BEt_2), 3.3 (s, 3H, OMe), 6.7 (s, 1H, =CH), 5.2 (t, 1H, =CH).

10.4.6.11. *Protodeborylation of 1-(vinyl)- and 1-(allyl)siloles **114c - P** and **116 - P***

Experimental procedure and afterwards work up was the same as adopted for siloles **102 - P** to **104 - P**.

114c - P: ^{1}H NMR (400 MHz): δ = 0.3 (s, 3H, Si-Me), 0.8, 2.3 (t, m, 5H, Et), 5.8 (dd, 1H, $^{2}J(^{1}H,^{1}H)$ = 3.5 Hz, $^{3}J(^{1}H,^{1}H)$ = 20.2 Hz, $=CH_2$), 5.9 (dd, 1H, $^{2}J(^{1}H,^{1}H)$ = 3.5 Hz,

$^3J(^1H,^1H)$ = 14.6 Hz, $=CH_2$), 6.2 (dd, 1H, $^3J(^1H,^1H)_{cis}$ = 14.6 Hz, $^3J(^1H,^1H)_{trans}$ = 20.5 Hz, Si-HC=), 7.0 - 7.2, 7.4 (m, m, 11H, C^4H, Ph).

116c - P: ^1H NMR (400 MHz): δ = 0.3 (s, 3H, Si-Me), 1.0, 2.3 (t, m, 5H, Et), 1.7 (d, 2H, $^3J(^1H,^1H)$ = 8.0 Hz, Si-CH_2), 4.7 (m, 1H, =CH), 5.6 (m, 2H, $=CH_2$), 7.1, 7.2, 7.4 (m, m, m, 11H, C^4H, Ph).

10.4.6.12. *Syntheses of 1,1-(divinyl)silole derivatives **119 - P** and **120 - P***

The experimental procedure and work up was the same as for siloles discussed above.

119a - P: ^1H NMR (400 MHz): δ = 0.8, 0.8, 1.2, 1.4, 2.2, 2.3 (t, t, m, m, t, t, 18H, Bu), 0.9, 2.1 (t, q, 5H, Et), 5.9 (dd, 1H, $^2J(^1H,^1H)$ = 4.1 Hz, $^3J(^1H,^1H)$ = 20.0 Hz, $=CH_2$), 5.9 (dd, 1H, $^2J(^1H,^1H)$ = 4.1 Hz, $^3J(^1H,^1H)$ = 14.8 Hz, $=CH_2$), 6.1 (dd, 1H, $^3J(^1H,^1H)$ = 14.8 Hz, $^3J(^1H,^1H)$ = 20.0 Hz, HC=), 6.4 (m, 1H, $^3J(^1H,^{29}Si)$ = 13.8 Hz, C^4H).

119c - P: ^1H NMR (400 MHz): δ = 0.9, 2.3 (t, q, 5H, Et), 5.9 (dd, 1H, $^2J(^1H,^1H)$ = 3.5 Hz, $^3J(^1H,^1H)$ = 20.1 Hz, $=CH_2$), 5.9 (dd, 1H, $^2J(^1H,^1H)$ = 3.5 Hz, $^3J(^1H,^1H)$ = 14.9 Hz, $=CH_2$), 6.2 (dd, 1H, $^3J(^1H,^1H)_{cis}$ = 14.8 Hz, $^3J(^1H,^1H)_{trans}$ = 20.0 Hz, HC=), 7.0 - 7.2, 7.3, 7.5 (m, m, m, 11H, Ph, C^4H).

120a - P: ^1H NMR (400 MHz): δ = 0.9, 1.3, 2.4 (t, m, t, 9H, Bu), 1.0, 2.3 (t, q, 5H, Et), 6.0 (dd, 1H, $^2J(^1H,^1H)$ = 3.9 Hz, $^3J(^1H,^1H)$ = 19.9 Hz, $=CH_2$), 6.1 (dd, 1H, $^2J(^1H,^1H)$ = 3.9 Hz, $^3J(^1H,^1H)$ = 15.0 Hz, $=CH_2$), 6.3 (dd, 1H, $^2J(^1H,^1H)$ = 15.1 Hz, $^3J(^1H,^1H)$ = 19.8 Hz, HC=), 7.2 (s, 1H, $^3J(^1H,^{29}Si)$ = 13.3 Hz, C^4H), 1.2, 7.3, 7.5 (s, m, m, 13H, 4-^{t}Bu-C_6H_4).

120e´ - P: ^1H NMR (400 MHz): δ = 6.6 (m, 1H, C^4H), other protons overlapped with silole **120a - P**.

11. LITERATURE CITED

1. D. E. Kaufmann, *in Science of Synthesis* 6 (**2004**) p.1.
2. I. Omae, "*Application of Organometallic Compounds*", *wiley* (**1998**) p. 92.
3. R. Köster, G. Seidel and B. Wrackmeyer, *Angew. Chem.* 106 (**1994**) 2380; *Angew. Chem. Int. Ed.* 33 (**1994**) 2294.
4. P. Idelmann, G. Müller, W. R. Scheidt, W. Schüßler and R. Köster, *Angew. Chem.* 96 (**1984**) 145; *Angew. Chem. Int Ed.* 23 (**1984**) 153.
5. R. Köster, S. Andrzej, W. Schüßler, D. Bläser and R. Boese, *Chem. Ber*. 127 (**1994**) 1191.
6. X.-C. Liu, J. L. Hubbard and W. H. Scouten, *J. Organomet. Chem.* 493 (**1995**) 91.
7. H. A. Ali, V. M. Dembitsky and M. Srebnik, "*Contemporary Aspects of Boron: Chemistry and Biological Applications*", *Elsevier* (**2005**).
8. H. Shimizu, S. Hara and A. Suzuki, *Syn. Comm.* 20 (**1990**) 549.
9. S. Hyuga, S. Hara and A. Suzuki, *Bull. Chem. Soc. Jpn.* 65 (**1992**) 2303.
10. (a) T. Ishiyama, S. Abe, N. Miyaura and A. Suzuki, *Chem. Lett.* 21 (**1992**) 691; (b) T.-Y. Luh, M.-K. Leung and K.-T. Wong, *Chem. Rev.* 100 (**2000**) 3187; (c) J. H. Kirchhoff, M. R. Netherton, I. D. Hills and G. C. Fu, *J. Am. Chem. Soc.*124 (**2002**) 13662; (d) C. Song, Y. Ma, Q. Chai, C. Ma, W. Jiang and M. B. Andrus, *Tetrahedron* 61 (**2005**) 7438; (e).G. H. Torres, S. Choppin and F. Colobert, *Eur. J. Org. Chem.* (**2006**) 1450.
11. (a) J. T. Clark, M. J. Rodezno, B. S. Clendenning, S. Aouba, M. P. Brodersen, J. A. Lough, E. H. Ruda and I. Manners, *Chem. Eur. J.* 11 (**2005**) 4526; (b) F. Jäkle, *Coord. Chem. Rev*. 250 (**2006**) 1107; (c) H. Y. Sehlleier, A. Verhoeven and M. Jansen, *J. Mat. Chem*. 17 (**2007**) 4316.
12. A. Suzuki, *Pure Appl. Chem.* 58 (**1986**) 629.
13. M. Carmen, A. Sánchez, M. J. Iglesias, J. G. Lopez, I. J. P. Álvarez and F. L. Ortiz, *Tetrahedron* 62 (**2006**) 3648.
14. H. J. M. Bowen, "*Environmental Chemistry of the Elements*", *Academic Press, New York* (**1979**).
15. (a) S. Patai and Z. Rappoport, (*Eds.*) "*The Chemistry of Organic Silicone Compounds*", *Wiley: New York,* (**1989**) p. 1242; (b) C. Chuit, R. J. P. Corriu, C. Reye and J. C. Young, *Chem. Rev*. 93 (**1993**) 1371; (c) A. Boudin, G. Cerveau,

C. Chuit, Robert J. P. Corriu and C. Reye, *Angew. Chem.* 98 (**1986**) 472; (d) A. Boudin, G. Cerveau, C. Chuit, R. J. P.Corriu and C. Reye, *Bull. Chem. Soc. Jpn.* 61 (**1988**) 101.

16. J.-L. Bréfort, R. J. P. Corriu, C. Guérin, B. J. L. Henner and W. W. C. W. C. Man, *Organometallics* 9 (**1990**) 2080.
17. (a) A. Sekiguchi, V. Y. Lee and M. Nanjo, *Coord. Chem. Rev.* 210 (**2000**) 11; (b) M. F.-Lappert, J. B. Pedley, J. Simpson and T. R. Spalding, *J. Organomet. Chem.* 29 (**1971**) 195; (c) S. Fukuzumi and T. Kitano, *J. Am. Chem. Soc.* 112 (**1990**) 3246; (d) S. Tsutsui, H. Tanaka, E. Kwon, S. Matsumoto and K. Sakamoto, *Organometallics* 23 (**2004**) 5659; (e) S. Matsumoto, S. Tsutsui, E. Kwon and K. Sakamoto, *Angew. Chem. Int. Ed.* 43 (**2004**) 4610.
18. (a) Y. Zhang, Y. Huang, X. Liu and Y. Yu, *J. Appl. Poly. Sci*. 89 (**2003**) 1702; (b) M. P. Achalpurkar, U. K. Kharul, H. R. Lohokare and P. B. Karadkar, *Sep. Purif. Technol*. 57 (**2007**) 304.
19. (a) Y. L. Liu, Y. C. Chiu and C. S. Wu, *J. Appl. Polym. Sci.* 87 (**2003**) 404; (b) C. Yang, A. Gu, H. Song, Z. X. Fang and L. Tong, *J. Appl. Polym. Sci.* 105 (**2007**) 2020; (c) F. H. Jancke, *J. Anal. Chem*. 342 (**1992**) 846.
20. (a) H. Aoki and T. Tokuda, *Macromol. Rapid. Commun.* 18 (**1997**) 31; (b) M. Itoh, K. Inoue, N. Hirayama, M. Sugimoto and T. Seguchi, *J. Mater. Sci*. 37 (**2002**) 3795.
21. R. Riedel, A. Kienzle, W. Dressler, L. Ruwisch, J. Bill and F. Aldinger, *Nature (London)* 382 (**1996**) 796.
22. J. Bill and F. Aldinger, *Adv. Mater*. 7 (**1995**) 775.
23. M. Weinmann, R. Haug, J. Bill, F. Aldinger, J. Schuhmacher and K. Müller, *J. Organomet. Chem.* 541 (**1997**) 345.
24. R. B. King, *"Inorganic Chemistry of Main Group Elelments", Wiley, New York,* (**1995**) p. 199.
25. H. Wieland, *Liebigs Ann. Chem.* 431 (**1923**) 30.
26. W. E. Davidsohn and M. C. Henry, *Chem. Rev*. 67 (**1967**) 73.
27. L. Brandsma, *"Synthesis of Acetylenes, Allenes, and Cumulenes-Methods and Techniques", Elsevier, Amsterdam* (**2004**).
28. L. Brandsma, *"Preparative Acetylenic Chemistry", Elsevier, Amsterdam,* 2nd ed. (**1988**).
29. B. Wrackmeyer, *Coord. Chem. Rev.* 145 (**1995**) 125.

30. J. E. Huheey (Ed. 3), *"Inorganic Chemistry-Principles of Structure and Reactivity", Harper International SI Edition, Cambridge* (**1983**).
31. W.-Y. Wong, C.-K. Wong, G.-L. Lu, K.-W. Cheah, J.-X. Shi and Z. Lin, *J. Chem. Soc*. *Dalton Trans*. (**2002**) 4587.
32. M. A. Bennett, C. J. Cobley, D. C. R. Hockless and T. Klettke, *Aust. J. Chem.* 52 (**1999**) 51.
33. (a). A. Ohff, S. Pulst, C. Lefeber, N. Peulecke, P. Arndt, V. V. Burkalov and U. Rosenthal, *Synlett*. (**1996**) 111; (b) U. Rosenthal, V. V. Burlakov, P. Arndt, W. Baumann and A. Spannenberg, *Organometallics* 22 (**2003**) 884; (c) A. Noor and R. Kempe, *Eur. J. Inorg. Chem.* 14 (**2008**) 2377.
34. Q. Zhou, X. Feng, L. Ni and J. Chen, *J. Appl. Polym. Sci.* 102 (**2006**) 2488.
35. (a) D. B. Wiley, G. Kaplan and T. Dobbins, *U.S. patent application No*. PCT/US2002/027126 (**2003**); (b) D. B. Wiley, G. Kaplan and T. Dobbins, *U.S. patent application No*. 20050076560 (**2005**).
36. W. Palitzsch, U. Böhme and G. Roewer, *J. Organomet. Chem.* 552 (**1998**) 213.
37. H. Lang, U. Lay and M. Weinmann, *J. Organomet. Chem.* 436 (**1992**) 265.
38. (a) H. Lang, U. Lay and L. Zsolnai, *J. Organomet. Chem.* 417 (**1991**) 377; (b) P.-M. Pellny, N. Peulecke, V. V. Burlakov, W. Baumann, A. Spannenberg and U. Rosenthal, *Organometallics* 19 (**2000**) 1198.
39. Z. Xi, R. Fischer, R. Hara, W.-H. Sun, Y. Obora, N. Suzuki, K. Nakajima and T. Takahashi, *J. Am. Chem. Soc.* 119 (**1997**) 12842.
40. W.-Y. Wong, C.-K. Wong and G.-L. Lu, *J. Organomet. Chem*. 671 (**2003**) 27.
41. H. Lang and U. Lay, *Z. Anorg. Allg. Chem*. 596 (**1991**) 7.
42. E. Klaus and A. Sebald, *Magn. Reson. Chem.* 32 (**1994**) 679.
43. H. C. Brown, *"Organic Syntheses via Boranes", Wiley, New York* (**1975**).
44. (a) H. C. Brown and B. C. S. Rao, *J. Org. Chem*. 22 (**1957**) 1136; (b) C. B. Fritschi, S. M. Wernitz, C. M. Vogels, M. P. Shaver, A. Decken, A. Bell and S. A. Westcott, *Eur. J. Inorg. Chem.* (**2008**) 779; (c) N. Miyaura and A. Suzuki, *Chem. Rev*. 95 (**1995**) 2457;.(d) R. Köster, G. Seidel, F. Lutz, C. Krüger, G. Kehr and B. Wrackmeyer, *Chem. Ber.* 127 (**1994**) 813.
45. B. Wrackmeyer, W. Milius, M. H. Bhatti and S. Ali, *J. Organomet. Chem.* 669 (**2003**) 72.

46. (a) J. A. Soderquist, J. C. Colberg and L. D. Valle, *J. Am. Chem*. Soc. 111 (**1989**) 4873; (b) K. Uchida, K. Utimoto and H. Nozaki, *J. Org. Chem*. 41 (**1976**) 2941; (c) K. Uchida, K. Utimoto and H. Nozaki, *Tetrahedron* 33 (**1977**) 2987.
47. (a) S. Rajagopalan and G. Zweifel, *Synthesis* (**1984**) 113; (b) J. A. Miller and G. Zweifel, *Synthesis* (**1981**) 288; (c) J. A. Miller and G. Zweifel, *J. Am. Chem. Soc.* 103 (**1981**) 6217.
48. R. Köster, G. Seidel, R. Boese and B. Wrackmeyer, *Z. Naturforsch.* 50b (**1995**) 439.
49. B. Wrackmeyer, H. Maisel, W. Milius, A. Badshah, E. Molla and A. Mottalib, *J. Organomet. Chem.* 602 (**2000**) 45.
50. B. Wrackmeyer, A. Badshah, E. Molla and A. Mottalib, *J. Organomet. Chem.* 584 (**1999**) 98.
51. (a) B. Wrackmeyer, O. L. Tok and Y. N. Bubnov, *J. Organomet. Chem.* 580 (**1999**) 234; (b) B. Wrackmeyer, O. L. Tok and W. Milius, *Appl. Organomet. Chem.* 20 (**2006**) 443; (c) B. Wrackmeyer, W. Milius and O. L. Tok, *Chem. Eur. J.* 9 (**2003**) 4732; (d) B. Wrackmeyer, K. Shahid and S. Ali, *Appl. Organomet. Chem.* 19 (**2005**) 377.
52. J. Dubac, A. Laporterie and G. Manuel, *Chem. Rev*. 90 (**1990**) 215.
53. E. Colomer, R. J. P. Corriu and M. Lheureux, *Chem. Rev*. 90 (**1990**) 265.
54. R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. D. Santos, J. L. Bredas, M. Logdlund and W. R. Salaneck, *Nature* (London) 397 (**1999**) 121.
55. G. Yu, S. Yin, Y. Liu, J. Chen, X. Xu, X. Sun, D. Ma, X. Zhan, Q. Peng, Z. Shuai, B. Tang, D. Zhu, W. Fang and Y. Luo, *J. Am. Chem. Soc*.127 (**2005**) 6335.
56. B. Wrackmeyer, *Heteroatom Chem.* 17 (**2006**) 188.
57. E. Braye, W. Hübel and I. Caplier, *J. Am. Chem. Soc.* 83 (**1961**) 4406.
58. J. B.-Wilking, Y. Zhang, J. Y. Corey and N. P. Rath, *J. Organomet. Chem.* 693 (**2008**) 1233.
59. R. Köster, G. Seidel, J. Süß and B. Wrackmeyer, *Chem. Ber.* 126 (**1993**) 1107.
60. B. Wrackmeyer, G. Kehr and J. Süß, *Chem. Ber*. 126 (**1993**) 2221.
61. B. Wrackmeyer, O. L. Tok, M. H. Bhatti and S. Ali, *Collect. Czech. Chem. Commun*. 67 (**2002**) 822.
62. D. A. Armitage, in C. W. Bird (Ed.), *"Comprehensive Heterocyclic Chemistry", Elsevier* (**1996**).

63. G. K. Henry, R. Shinimoto, Q. Zhou and W. P. Weber, *J. Organomet. Chem.* 350 (**1988**) 3.
64. M. Kako, S. Oba, R. Uesugi, S. Sumiishi, Y. Nakadaira, K. Tanaka and T. Takada, *J. Chem. Soc. Perkin trans*. 2 (**1997**) 1251.
65. K.-I. Kanno and M. Kira, *Chem. Lett.* (**1999**) 1127.
66. B. Wrackmeyer and J. Süß, *Z. Naturforsch.* 57b (**2002**) 741.
67. B. Wrackmeyer, O. L. Tok, K. Shahid and S. Ali, *Inorg. Chim. Acta* 357 (**2004**) 1103.
68. B. Wrackmeyer, O. L. Tok and R. Kempe, *Inorg. Chim. Acta* 358 (**2005**) 4183.
69. B. Wrackmeyer, O. L. Tok, W. Milius, A. Khan and A. Badshah, *Appl. Organomet. Chem*. 20 (**2006**) 99.
70. B. Wrackmeyer, H. E. Maisel, E. Molla, A. Mottalib, A. Badshah, M. H. Bhatti and S. Ali, *Appl. Organomet. Chem.* 17 (**2003**) 465.
71. P. Binger and R. Köster, *Synthesis* (**1973**) 309.
72. P. Binger and R. Köster, *Tetrahed. Lett.* 6 (**1965**) 1901.
73. J. A. Soderquist and B. Santiago, *Tetrahedron Lett.* 31 (**1990**) 5113.
74. (a) R. Köster, *Pure Appl. Chem*. 49 (**1977**) 765; (b) R. Köster, G. Seidel, R. Boese and B. Wrackmeyer, *Chem. Ber.* 120 (**1987**) 669; (c) R. Köster, G. Seidel, B. Wrackmeyer, K. Horchler and D. Schlosser, *Angew. Chem*. 101 (**1989**) 945; *Angew. Chem. Int. Ed.* 28 (**1989**) 918; (d) R. Köster, G. Seidel and B. Wrackmeyer, *Chem. Ber.* 122 (**1989**) 1825.
75. B. Wrackmeyer, O. L. Tok, M. H. Bhatti and S. Ali, *Appl. Organomet. Chem*. 17 (**2003**) 843.
76. B. Wrackmeyer, W. Milius, M. H. Bhatti and S. Ali, *J. Organomet. Chem*. 665 (**2003**) 196.
77. S. Bayer, PhD dissertation Universität Bayreuth, Bayreuth Germany (**2005**).
78. R. Köster (Ed), *"Methoden der Organischen Chemie",* Vol. 13, 3c, *Thieme, Stuttgart* (**1986**) p. 231-244.
79. M. Hoshi, Y. Masuda and A. Arase, *Bull. Chem. Soc. Jpn*. 58 (**1985**) 1683.
80. J. Süß, PhD dissertation Universität Bayreuth, Bayreuth Germany (**1995**).
81. B. Wrackmeyer and O. L. Tok, *Z. Naturforsch.* 61b (**2006**) 243.
82. O. N. Florensova, B. A. Sokolov and L. I. Volkova, *Izv. Akad. Nauk SSSR, Ser. Khim.* (**1973**) 1390.

83. H. Matsumoto, T. Kato, I. Matsubara, Y. Hoshino and Y. Nagai, *Chem. Lett.* (**1979**) 1287.
84. G. Deleris, J. Dunogues, R. Calas and P. Lapouyade, *J. Organomet. Chem.* 80 (**1974**) C45.
85. B. Wrackmeyer, K. Shahid and S. Ali, *Z. Naturforsch.* 60b (**2005**) 590.
86. H. Q. Liu and J. F. Harrod, *Can. J. Chem.* 68 (**1990**) 1100.
87. L. Guo, J. D. Bradshaw, D. B. McCoville, C. A. Tessier and W. J. Youngs, *Organometallics* 16 (**1997**) 1685.
88. B. Wrackmeyer, B. H. K.-Hofmann, W. Milius, P. Thoma, O. L. Tok and M. Herberhold, *Eur. J. Inorg. Chem.* (**2006**) 101.
89. (a) K. Takaki, M. Kurioka, T. Kamata, K. Takehira, Y. Makioka and Y. Fujiwara, *J. Org. Chem.* 63 (**1998**) 9265; (b) M. Itoh, M. Mitsuzuka, T. Utsumi, K. Iwata and K. Inoue, *J. Organomet. Chem*. 476 (**1994**) C30.
90. C. Kim, K. Jeong and I. Jung, *J. Polym. Sci., Part A: Polym. Chem.* 38 (**2000**) 2749.
91. (a) M. A. Brook, B. Ramacher, C. Dallaire, H. K. Gupta, D. Ulbrich and R. Ruffolo, *Inorg. Chim. Acta* 250 (**1996**) 49; (b) C. Kim and M. Kim, *J. Organomet. Chem.* 563 (**1998**) 43.
92. B. Wrackmeyer, W. Milius and A. Badshah, *J. Organomet. Chem.* 656 (**2002**) 97.
93. H. Schmidbaur, J. Ebenhöch and G. Müller, *Z. Naturforsch.* 43b (**1988**) 49.
94. B. Wrackmeyer, H. E. Maisel, J. Süß and W. Milius, *Z. Naturforsch.* 51b (**1996**) 1320.
95. (a) H. C. Brown and M. V. Bhatt, *J. Am. Chem. Soc.* 88 (**1966**) 1440; (b) R. Köster (Ed), *"Methoden der Organischen Chemie",* Vol. 13, 3c, *Thieme, Stuttgart* (**1982**) p. 217.
96. E. Abuin, J. Groteword, E. A. Lissi and M. C. Vara, *J. Chem. Soc. B* (**1968**) 1044.
97. B. Wrackmeyer, *Progr. NMR Spectrosc.* 12 (**1979**) 227.
98. B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.* 20 (**1988**) 61.
99. M. Yalpani, R. Köster and R. Boese, *Chem. Ber.* 125 (**1992**) 15.
100. M. Itoh, A. Arase, K. Suzuki and A. Suzuki, *Kogyo Kagaku Zasshi,* 71 (**1968**) 1653.

101. (a) R. Köster and W. Larbig, *Angew. Chem*. 73 (**1961**) 620; (b) R. Köster, W. Larbig and W. G. Rotermund, *Liebigs Ann. Chem*. 682 (**1963**) 21.
102. (a) B. Wrackmeyer, E. Khan, S. Bayer and K. Shahid, *Z. Naturforsch.* 62b (**2007**) 1174; (b) B. Wrackmeyer, E. Khan and W. Milius, *Z. Naturforsch.* 63b (**2008**) submitted.
103. (a) R. Köster, G. Benedikt, W. Larbig, K. Reinert and G. Rotermund, *Angew. Chem.* 75 (**1963**) 1079; (b) R. Köster, W. Larbig and G. W. Rotermund, *Liebigs Ann. Chem.* 682 (**1965**) 21.
104. P. H. M. Budzelaar and G. Talarico, *Structure and Bonding* 105 (**2003**) 141.
105. E. Iglesia, D. G. Barton, S. L. Soled, S. Miseo, J. E. Baumgartner, W. E. Gates, G. A. Fuentes and G. D. Meitzner, *Studies in Surface Science and Catalysis* 101 (**1996**) 533.
106. R. Köster, G. Bruno and P. Binger, *Liebigs Ann. Chem*. 644 (**1961**) 1.
107. B. Wrackmeyer, *Annu. Rep. NMR spectrosc.* 57 (**2006**) 1.
108. (a) J. K. M. Sanders and B. K. Hunter (2nd Ed.), "*Modern NMR Spectroscopy"*, *Oxford University Press, Oxford* (U.K.) (**1993**) Chapter 6; (b) K. Stott, J. Keeler, Q. N. Van and A. J. Shaka, *J. Magn. Reson.* 125 (**1997**) 302.
109. E. Kupce and E. Lukevics in "*Isotopes in the Physical and Biomedical Sciences"*, Vol. 2: (Eds.: E. Buncel, J. R. Jones) "*Isotopic Applications in NMR Studies"*, *Elsevier, Amsterdam (The Netherlands)* (**1991**) pp. 213–295.
110. H. Nöth and B. Wrackmeyer, "*Nuclear Magnetic Resonance Spectroscopy of Boron Compounds"*, (Eds.: P. Diehl, E. Fluck, R. Kosfeld), "*NMR-Basic Principles and Progress"*, Vol. 14, *Springer, Berlin (Germany)* (**1978**)**.**
111. B. Wrackmeyer, E. Khan and R. Kempe, *Appl. Organomet. Chem.* 21 (**2007**) 39.
112. B. Wrackmeyer, E. Khan and R. Kempe, *Z. Naturforsch.* 62b (**2007**) 75.
113. H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.* 85 (**1963**) 2063.
114. T. F. O. Lim, J. K. Myers, T. Greg and P. R. Jones, *J. Organomet. Chem.* 135 (**1977**) 249.
115. (a) M. Gastreich, C. M. Marian, H. Jüngermann and M. Jansen, *Eur. J. Inorg. Chem*. (**1999**) 75; (b) M. Weinmann, T. W. Kamphowe, P. Fischer and F. Aldinger, *J. Organomet. Chem.* 592 (**1999**) 115.
116. (a) L. M. Ruwisch, P. Dürichen and R. Riedel, *Polyhedron* 19 (**2000**) 323; (b) N. G. Bhat and M. A. Villanueva, *J. Organomet. Chem.* 691 (**2006**) 1298.

117. J. Schraml (Ed. Rappoport Z and Apeloig Y), "*The Chemistry of Organic Silicon Compounds"*, vol. 3, *Wiley, Chichester* (**2001**) p 223-339.
118. (a) G. A. Morris and R. Freeman, *J. Am. Chem. Soc.* 101 (**1979**) 760; (b) D. P. Burum and R. R. Ernst, *J. Magn. Reson.* 39 (**1980**) 163.
119. R. Köster, G. Seidel, I. Klopp, C. Krüger, G. Kehr, J. Süß and B. Wrackmeyer, *Chem. Ber.* 126 (**1993**) 1385.
120. M. J. S. Dewar, "*Hyperconjugation"*, *Ronald Press, New York* (**1962**).
121. R. Boese, D. Bläser, N. Niederprüm, M. Nüsse, W. A. Brett, P. R. Schleyer, M. Bühl and N. J. R. van Eikema Hommes, *Angew. Chem.* 104 (**1992**) 352; *Angew. Chem. Int. Ed*. 31 (**1992**) 314.
122. I. V. Alabugin and T. A. Zeidan, *J. Am. Chem. Soc*. 124 (**2002**) 3175.
123. B. Wrackmeyer and O. L. Tok, *Z. Naturforsch.* 60b (**2005**) 259.
124. C. A. Brown, R. A. Coleman, *J. Org. Chem*. 44 (**1979**) 2328.
125. C. Wang, Q. Luo, H. Sun, X. Guo and Z. Xi, *J. Am. Chem. Soc.* 129 (**2007**) 3094.
126. B. Wrackmeyer, U. Klaus, W. Milius, E. Klaus and T. Schaller, *J. Organomet. Chem.* 517 (**1996**) 235.
127. S. Yamaguchi, K. Iimura, and K. Tamao, *Chem. Lett.* (**1998**) 89.
128. H.-J. Son, W.-S. Han, J.-Y. Chun, C.-L. Lee, J.-I. Han, J. Ko and S. O. Kang, *Organometallics* 26 (**2007**) 519.
129. B. Wrackmeyer, S. Kundler, W: Milius and R. Boese, *Chem. Ber.* 127 (**1994**) 333.
130. R. Köster, G. Seidel and B. Wrackmeyer, *Chem. Ber*. 122 (**1989**) 1825.
131. B. Wrackmeyer, J. Süß and W. Milius, *Chem. Ber.* 129 (**1996**) 147.
132. (a) J. A. Soderquist, K. Matos and J. Ramos, *Tetrahedron Lett.* 36 (**1995**) 2401; (b) J. A. Soderquist, A. M. Rane, K. Matos and J. Ramos, *Tetrahedron Lett.* 36 (**1995**) 6847.
133. A. Fürstner and G. Seidel, *Tetrahedron* 51 (**1995**) 11165.
134. K. Matos and J. A. Soderquist, *J. Org. Chem.* 63 (**1998**) 461.
135. R. Köster (Ed.), *"Methoden der Organischen Chemie",* Vol. 13, 3c, *Thieme, Stuttgart* (**1982**) p. 495.
136. R. Köster, G. Seidel, D. Blaeser and R. Boese, *Z. Naturforsch.* 49b (**1994**) 370.
137. R. Anulewicz-Ostrowska, S. Lulinski and J. Serwatowski, *Inorg. Chem*. 38 (**1999**) 3796.

138. W. J. Bobear, *Patent Application: US* 69-849279 19690805, USA (**1970**).
139. S. Yajima. K. Okamura, T. Shishido and Y. Hasegawa, *Patent Application: DE* 79-2918549 19790508, Germany (**1979**).
140. S. Hoshii, A. Kojima and S. Otani, *J. Mat. Sci. Lett*. 19 (**2000**) 169.
141. B. Wrackmeyer and R. Köster, *Chem. Ber*. 115 (**1982**) 2022.
142. R. Köster, G. Seidel, D. Blaeser and R. Boese, *Z. Naturforsch.* 49b (**1994**) 377.
143. H. Schumann, A. Heim, J. Demtschuk and S. H. Mühle, *Organometallics,* 22 (**2003**) 118.
144. (a) B. Wrackmeyer, U. Dörfler, G. Kehr, H. E. Maisel and W. Milius, *J. Organomet*. *Chem*. 524 (**1996**) 169; (b) B. Wrackmeyer, H. E. Maisel, W. Milius, M. H. Bhatti and S. Ali, *Z. Naturforsch.* 58b (**2003**) 543.
145. M. A. Beckett, D. E. Hibbs, M. B. Hursthouse, K. M. A. Malik, P. Owen and K. S. Varma, *J. Chem. Crystallogr*. 28 (**1998**) 277.
146. (a) S. Shambayati, S. L. Schreiber, J. F. Blake, S. G. Wierschke and W. L. Jorgensen, *J. Am. Chem. Soc.* 112 (**1990**) 697; (b) P. D. Lickiss, S. A. Litster, A. D. Redhouse and C. J. Wisener, *Chem. Commun.* (**1991**) 173; (c) W. Wojnowski, B. Becker, K. Peters, E. M. Peters and H. G. von Schnering, *Z. Anorg. Allg. Chem*. 562 (**1988**) 17; (d) I. L. Karle, J. M. Karle and C. J. Nielson, *Acta Crystallogr. Section C*, 42 (**1986**) 64; (e) A. I. Gusev, M. Yu. Antipin, D. S. Yufit, Yu. T. Struchkov, V. D. Sheludyakov, V. I. Zhun and S. D. Vlasenko, *Zh. Strukt. Khim*. 24 (**1983**) 178; (f) M. G. Voronkov, D. Yu. Nesterov, A. I. Gusev, N. V. Alekseev and M. B. Lotarev, *Dokl. Akad Nauk SSSR* 257 (**1981**) 1377.
147. E. Lukevics, V. Dirnens, P. Arsenyan, J. Popelis and A. Kemme, *Main Group Met. Chem.* 19 (**1996**) 167.
148. (a) C. A. Ernst, A. L. Allred, M. A. Ratner, M. D. Newton, G. V. Gibbs and J. W. Moskowitz, *Chem. Phys. Lett.* 81 (**1981**) 424; (b) A. V. Belyakov, A. Haaland, D. E. Shorokhov, H. V. Volden and R. West, *Russ. J. Gen. Chem*. 69 (**1999**) 235; (c) A. I. Ermakov and A. E. Merkulov, *Zh. Strukt. Khim*. 39 (**1998**) 624.
149. F. Tielens, F. de-Proft and P. Geerlings, *THEOCHEM* 542 (**2001**) 227.
150. (a) A. Berenbaum, A. J. Lough and I. Manners, *Acta Crystallogr. Section E* 58 (**2002**) 562; (b) B. Wrackmeyer, A. Ayazi, W. Milius and M. Herberhold, *J. Organomet. Chem.* 682 (**2003**) 180.
151. B. Wrackmeyer, C. Bihlmayer and M. Schilling, *Chem. Ber.* 116 (**1983**) 3182.
152. B. Wrackmeyer, *J. Organomet. Chem*. 205 (**1981**) 1.

153. B. Wrackmeyer, U. Dörfler, G. Kehr, H. E. Maisel and W. Milius, *J. Organometal. Chem.* 524 (**1996**) 169.
154. H. Nöth and B. Wrackmeyer, "*Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*", Springer-Verlag Berlin (**1978**) p 19.
155. A. D. Negro, L. Ungaretti and A. Perotti, *J. Chem. Soc. Dalton Trans*. (**1972**) 1639.
156. B. Wrackmeyer, E. Khan and R. Kempe, *Z. Anorg. Allg. Chem.* 633 (**2007**) 453.
157. M. Yalpani, R. Boese, K. Seevogel and R. Köster, *J. Chem. Soc. Dalton Trans.* (**1993**) 47.
158. A. Lang, H. Nöth and M. Schmidt, *Chem. Ber.* 128 (**1995**) 751.
159. (a) G. W. Kramer and H. C. Brown, *J. Organomet. Chem*. 132 (**1977**) 9; (b) G. W. Kramer and H. C. Brown, *J. Org. Chem.* 42 (**1977**) 2292.
160. B. Wrackmeyer, E. Khan and R. Kempe, *Appl. Organomet. Chem.* 22 (**2008**) 383.
161. B. Wrackmeyer, E. Khan and R. Kempe, *Z. Naturforsch.* 63b (**2008**) 275.
162. H. Binder, W. Mathies, H. J. Deiseroth and F. Han, *Z. Naturforsch*.**1984**, 39b, 1717.
163. B. Wrackmeyer, G. Kehr, J. Subb and E. Molla, *J. Organomet. Chem*. 577 (**1999**) 82.
164. R. Köster, G. Seidel and B. Wrackmeyer, *Chem. Ber.* 124 (**1991**) 1003.
165. R. Köster (Ed.), "*Methoden der Organischen Chemie*", Vol. 13, 3a, *Thieme, Stuttgart* (**1982**) p. 145.
166. T. Kottke and D. Stalke, *J. Appl. Crystallogr.* 26 (**1993**) 615.
167. A. Altomare, C. M. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, G. G. A. Moliterni, G. Polidori and R. Spagna, *J. Appl.Crystallogr.* 32 (**1999**) 115.
168. M. G. Sheldrick *SHELX-97*, Program for Crystal Structure Analysis (Release 97-2). Institut für Anorganische Chemie der Universität, Göttingen (**1998**).
169. J. L. Farrugia, *J. Appl. Crystallogr.* 32 (**1999**) 837.
170. S. T. Liddle and W. Clegg, *J. Chem. Soc., Dalton Trans.* (**2001**) 402.

12. LIST OF PUBLICATIONS

Part of work done during the course of this dissertation has been published in the following papers.

1. Ezzat Khan, Stefan Bayer, Bernd Wrackmeyer, *Z. Naturforsch.* 64b (**2009**) 47. "Reactivity of Triethylborane towards Dialkyn-1-yl(chloro)silanes. Competition between 1,1-Organoboration and 1,2-Hydroboration."
2. Ezzat Khan, Bernd Wrackmeyer, Rhett Kempe, *Eur. J. Inorg. Chem.* (**2008**) 5367. "Combination of 1,2-Hydroboration and 1,1-Organoboration. A Convenient Route to New 5-Silaspiro[4,4]nona-1,6-diene Derivatives"
3. Bernd Wrackmeyer, Ezzat Khan, Wolfgang Milius, *Z. Naturforsch.* 63b (**2008**) 1267. "1,2-Hydroboration of Alkyn-1-yldichlorosilanes using Triethylborane"
4. Bernd Wrackmeyer, Ezzat Khan, Rhett Kempe, *Appl. Organomet. Chem.* 22 (**2008**) 383. "Synthesis and structure of novel spirosilanes. Combination of 1,2-hydroboration and 1,1-organoboration"
5. Bernd Wrackmeyer, Ezzat Khan, Rhett Kempe, *Z. Naturforsch.* 63b (**2008**) 275. "Protodeborylation of Triorganoboranes"
6. Bernd Wrackmeyer, Ezzat Khan, Rhett Kempe, *Appl. Organomet. Chem.* 21 (**2007**) 39. "Boryl-substituted 1-silacyclobutenes. Formation and molecular structure"
7. Bernd Wrackmeyer, Ezzat Khan, Rhett Kempe, *Z. Naturforsch.* 62b (**2007**) 75. "1,2-Hydroboration of Alkyn-1-yl(chloro)silanes: Alkenes Bearing Chlorosilyl and Dialkylboryl Groups in Geminal Positions"
8. Bernd Wrackmeyer, Ezzat Khan, Rhett Kempe, *Z. Anog. Allgem. Chem.* 633 (**2007**) 453. "Hydrolysis and Oxidation of a 1-Boryl-1-silyl-alkene. Molecular Structures of 9-Hydroxy-9-borabicyclo[3.3.1]nonane and a Bicyclic Oxasilabora-heptadecane $B_2(OSiPh_2OSiPh_2O)_3$"
9. Bernd Wrackmeyer, Ezzat Khan, Stefan Bayer, Khadija Shahid, *Z. Naturforsch.* 62b (**2007**) 1174. "Triethylborane: an "Old" Reagent with New Functions. 1,2-Hydroboration"

13. NMR AND X-RAY DATA TABLES

Table 2.1. ^{13}C and ^{29}Si NMR data [a] of alkyn-1-yl(chloro)silanes **1 - 3**.

	$\delta^{13}C(\equiv C)$	$\delta^{13}C(Si\text{-}C\equiv)$	$\delta^{13}C(Si\text{-}Ph)$	$\delta^{29}Si$
1a [b]	111.7 [21.2]	79.0 [109.8]	132.4 [85.7], 135.0, 128.4, 130.4 (*i, o, m, p*)	-36.3
1c [c]	121.2 [21.9]	85.7 [110.1]	133.2 [88.7], 134.1, 128.3, 129.4 (*i, o, m, p*)	-29.9
2a [d]	112.3 [21.3]	79.4 [110.7]	134.4 [86.4], 133.5, 128.2, 130.8 (*i, o, m, p*)	-10.4
2c [e]	108.5 [21.3]	88.2 [107.8]	133.8 [87.5, *i*]	-9.3
3a [f]	113.8 [22.2]	78.1 [114.4]	133.0 [80.2],134.3, 128.0, 130.8 (*i, o, m, p*)	-20.0
3c [g]	110.2 [28.0]	87.3 [118.1]	132.8 [89.5], 134.7, 128.5,129.8 (*i, o, m, p*)	-19.1

[a] Measured in $CDCl_3$ at 23 °C, some $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$ coupling constant values [±0.4 Hz] are given in square brackets; [b] measured in C_6D_6, Other ^{13}C data: δ = 30.8, 20.1, 19.9, 13.9 (Bu); [c] Other ^{13}C data: δ= 121.3, 132.3, 128.3, 131.4 (*i, o, m ,p*, Ph); [d] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 3.0 [67.7, Si-Me], 30.2, 21.9, 19.6, 13.5 (Bu); [e] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 2.8 [67.1, Si-Me], 121.6 (*i*), 133.5, 132.2, 130.9, 129.6, 128.3, 128.2 (Ph, Si-Ph); [f] Other ^{13}C data: δ = 30.1, 21.9, 19.7, 13.5 (Bu); [g] Other ^{13}C data: δ = 121.8, 131.1, 128.6, 132.6 (*i, o, m, p,* Ph).

Table 2.2. ^{13}C and ^{29}Si NMR data [a] of alkyn-1-yl(dichloro)silanes and alkyn-1-yl(trichloro)silanes **5 - 7.**

	$\delta^{13}C(\equiv C)$	$\delta^{13}C(Si\text{-}C\equiv)$	$\delta^{13}C(Si\text{-}R^1)$	$\delta^{29}Si$
5a [b]	112.5 [26.1]	79.2 [133.8]	7.4 [80.1]	-8.4
5c [c]	108.5 [27.3]	87.4 [131.3]	7.0 [75.8]	-7.1
6a [d] [e]	114.0 [27.4]	77.5 [139.6.]	133.1 [81.3], 133.3, 128.3, 128.6 (*i, o, m, p*)	-20.6
6b [f]	121.8 [26.8]	76.2 [138.9]	132.7, 133.6, 128.6, 132.1 (*i, o, m, p*)	-19.8
6c [g] [e]	107.8 [28.7]	86.8 [139.9]	134.7 [85.0], 132.4, 128.3, 129.0 (*i, o, m, p*)	-17.4
7a [h]	114.1 [35.5]	77.7 [177.6]	$SiCl_3$	-32.0
7c [i]	109.6 [35.1]	85.4 [175.4]	$SiCl_3$	-30.6

[a] Measured in C_6D_6, some $J(^{13}C,^{29}Si)$ spin-spin coupling constants (in Hz) are given in square brackets, NMR data correspond to silanes **4a** and **4c** are given in ref. [77]. [b] Other ^{13}C data: δ = 29.9, 22.1, 19.5, 13.6 (Bu); [c] Other ^{13}C data: δ = 120.8, 132.6, 128.6, 130.3 (*i, o, m, p*, Ph); [d] Other ^{13}C data: δ = 29.8, 21.9, 19.6, 13.5 (Bu); [e] Measured in $CDCl_3$; [f] Other ^{13}C data: δ = 28.5, 30.0 (^{t}Bu); [g] Other ^{13}C data: δ = 122.3, 129.3, 128.2, 130.6 (*i, o, m, p*, Ph); [h] Other ^{13}C data: δ = 29.6, 22.1, 19.4, 13.6 (Bu); [i] Other ^{13}C data: δ = 119.6, 132.9, 128.6, 131.0 (*i, o, m, p*, Ph).

Table 2.3. ^{13}C and ^{29}Si NMR data [a] for starting silanes **8 - 10**.

	$\delta^{13}C(\equiv C)$	$\delta^{13}C(Si\text{-}C\equiv)$	$\delta^{13}C(=CH_2)$	$\delta^{13}C(Si\text{-}CH=)$	$\delta^{29}Si$
8a [b]	111.8 [21.3]	79.6 [112.5]	135.5	134.6 [84.4]	-12.8
8b [c]	119.5 [21.1]	77.6 [110.1]	135.4	134.6 [84.4]	-12.6
8c [d]	108.6 [21.8]	88.6 [107.2]	136.1	133.8 [84.8]	-11.8
9a [e]	113.6 [22.3]	78.3 [114.8]	137.1	133.1 [86.8]	-21.9
9c [f]	110.2 [21.7]	87.3 [112.3]	137.8	134.5 [85.2]	-20.9
10a [g]	113.9 [28.0]	77.7 [139.8]	137.8	132.3 [104.1]	-22.3
10c [h]	109.7 [27.6]	85.9 [137.4]	138.5	131.7[104.5]	-21.2

[a] Measured in C_6D_6, coupling constants $J(^{13}C,^{29}Si)$ [$\pm$ 0.4 Hz] are given in square brackets; [b] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 2.6 [67.2, Si-Me], 30.4, 22.1, 19.7, 13.6

(Bu); [c] Other ^{13}C data: δ [J(^{13}C,^{29}Si)] = 2.7 [67.2, Si-Me], 30.5, 28.4 (^{t}Bu); [d] Other ^{13}C data: δ [J(^{13}C,^{29}Si)] = 2.3 [67.5, Si-Me], 122.1, 132.4, 129.6, 128.6 (*i, o, p, m*, Ph); [e] Other ^{13}C data: δ [J(^{13}C,^{29}Si)] = 30.3, 22.1, 19.8, 13.7 (Bu), 133.2 [89.1], 134.4, 128.4, 131.2 (*i, o, m, p*, Si-Ph); [f] Other ^{13}C data: δ [J(^{13}C,^{29}Si)] = 132.6 [88.7, *i*], 121.8 (*i*), 131.3, 129.8, 132.53, 132.45 128.6, 128.6 (Ph and Si-Ph); [g] Other ^{13}C data: δ = 29.8, 22.0, 19.5, 13.5 (Bu); [h] Other ^{13}C data: δ = 120.7, 132.7, 128.7, 130.5 (*i, o, m, p,* Ph).

Table 2.4. ^{13}C and ^{29}Si NMR spectroscopic data [a] of silanes **11 - 14**.

	δ^{13}C(≡C)	δ^{13}C(Si-C≡)	δ^{13}C(Si-R^1/Ph)	δ^{29}Si
11a [b] [d]	109.7 [20.4]	79.0 [102.3]	-1.9 [61.6]	-63.5
11c [b] [e]	107.9 [19.9]	87.9 [100.4]	-2.4 [62.3]	-61.0
11d [c] [f]	108.2 [20.2]	87.3 [100.9]	-2.3 [62.1]	-61.2
12a [g]	111.4 [20.1]	76.8 [105.5]	131.8 [81.6], 134.5, 128.0, 130.0 (*i o m, p*)	-65.5
12c [h]	108.5 [20.2]	85.6 [104.4]	130.8 [83.8], 135.2, 128.7, 129.5 (*i, o, m, p*)	-63.6
13a [b] [i]	110.0 [19.9]	80.8 [103.5]	0.9 [63.2]/135.9 [81.3], 134.4, 128.2, 130.0 (*i, o, m, p*)	-45.7
13c [b] [j]	108.1 [19.8]	89.8 [101.2]	0.2 [63.8]/134.6 [82.5], 134.6, 128.5, 130.4 (*i, o, m, p*)	-43.5
14a[k]	111.8 [22.0]	79.6 [107.3]	134.8 [82.7], 135.3, 128.3, 130.2 (*i, o, m, p*)	-49.2

[a] Measured in $CDCl_3$ at 23 °C; [b] measured in C_6D_6; [c] measured in THF-D_8; [d] Other ^{13}C data: δ = 30.7, 22.2, 19.9, 13.7 (Bu); [e] Other ^{13}C data: δ = 122.8, 132.4, 128.5, 129.3 (*i, o, m, p*, Ph); [f] Other ^{13}C data: δ = 21.3, 119.9, 129.3, 132.4, 139.4 (Me*, i, o, m, p*, 4-Me-C_6H_4); [g] Other ^{13}C data: δ = 30.3, 21.9, 19.8, 13.6 (Bu); [h] Other ^{13}C data: δ = 122.5, 132.5, 128.5, 130.9 (*i, o, m, p*, Ph); [i] Other ^{13}C data: δ = 30.7, 22.2, 19.9, 13.7 (Bu); [j] ^{13}C and ^{1}H data already reported [86186]; [k] Other ^{13}C data: δ = 30.6, 22.2, 20.0, 13.6 (Bu).

Table 2.5. NMR data (^{13}C and ^{29}Si) [a] of alkyn-1-yl(chloro)silanes **15 - 18**.

	δ^{13}C(≡C)	δ^{13}C(Si-C≡)	δ^{13}C(R)	δ^{29}Si
15a [b]	112.5 [25.9]	77.4 [125.8]	30.1, 22.1, 19.7, 13.6	-57.5
15c [b]	109.5 [25.5]	85.5 [124.3]	121.3, 128.5, 132.6, 130.1 (*i, o, m, p*)	-55.4
16a [c]	110.8 [24.9]	80.1 [122.8]	30.2, 22.1, 19.6, 13.6	-34.9
16c [d]	108.1 [24.5]	88.3 [121.3]	121.8, 132.6, 128.5, 129.8 (*i, o, m, p*)	-32.7
17c [e]	109.6 [25.2]	87.2 [126.1]	121.5, 132.7, 128.5, 130.0 (*i, o, m, p*)	-42.0.
18a	112.7 [31.7]	78.7 [157.8]	29.7, 22.0, 19.5, 13.5	-48.8

[a] Measured in C_6D_6; coupling constants $J(^{13}C,^{29}Si)$ [± 0.4 Hz] are given in brackets; [b] data taken from reference [77] for comparison; [c] Other ^{13}C data: δ [$^1J(^{13}C,^{29}Si)$] = 5.1 [73.7, Si-Me]; [d] Other ^{13}C data: δ [$^1J(^{13}C,^{29}Si)$] = 4.6 [74.8, Si-Me]; [e] Other ^{13}C data: δ [$^1J(^{13}C,^{29}Si)$] = 132.6 [99.7], 134.4, 128.7, 131.8 (*i, o, m, p*, Si-Ph).

Table 2.6. Crystal data and structure refinement for **13c.**

Formula	$C_{23}H_{18}Si$	Formula weight	322.46
Crystal	Long platelet	Dimensions [mm]	0.35x0.18x0.12
Crystal system	Monoclinic	Space group	P2(1)/c
Temperature [K]	293(2)	*Z*	8
Lattice parameters		Absorption coef. [mm^{-1}]	0.125
a [pm]	3678.0(7)	Measuring range [°]	2.4–26.1
b [pm]	597.79(12)	Volume [$Å^3$]	3750.6 (13)
c [pm]	1727.1(4)	Density [Mg/m^3]	1.142
$\alpha = \gamma$ [°]	90.00		
β [°]	99.00(3)		
Completeness to θ	26.1°:91.8 %	Goodness-of-fit on F^2	0.664
F(000)	1360	Reflections collected	20571
Refined parameters	433	Reflections with $I>2\sigma(I)$	6844
Diffractometer	STOE IPDS I	Wave length [pm]	71.073
wR_2/R_1 [$I>2\sigma(I)$]	0.0459/0.112	Max./min. Residual electron density [$epm^{-3}x10^{-6}$]	0.164/-0.113

Table 2.7. ^{13}C and ^{29}Si NMR data [a] of silanes **19 - 21.**

	$\delta^{13}C$(≡C)	$\delta^{13}C$(Si-C≡)	$\delta^{13}C$(=CH)	$\delta^{13}C$(Si-C=)	$\delta^{29}Si$
19a [b]	109.4 [20.0]	80.4 [103.4]	134.0	135.4 [79.4]	-48.4
19c [c]	107.7 [19.6]	89.4 [101.2]	135.4	134.0 [80.4]	-46.2
20a [d]	111.3 [20.2]	79.1 [107.2]	135.5	134.3 [80.4]	-51.8
20c [e]	109.1 [20.1]	88.0 [105.3]	136.9	135.1 [81.0]	-50.0
21c [f]	107.4 [18.7]	89.8 [98.8]	24.2 [58.7], 115.5, 132.9 (Allyl)		-39.9

[a] Measured in C_6D_6, $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$ are given in square brackets; [b] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 0.03 [63.3, Si-Me], 30.7, 22.1, 19.8, 13.7 (Bu); [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 0.5 [63.9, Si-Me], 123.0 [2.1], 132.4, 128.5, 129.2 (*i, o, m, p,* Ph); [d] Other ^{13}C data: δ = 30.6, 22.1, 19.9, 13.7 (Bu), 137.1, 134.9, 128.3, 130.2 (*i, o, m, p,* Si-Ph); [e] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 132.9 [84.1, *i*], 122.6 (*i*, ≡C-Ph), 132.7, 132.4, 130.7, 129.4, 128.6, 128.6 (Ph and Si-Ph); [f] Other ^{13}C data: δ = 115.5, 132.4, 128.5, 129.1 (*i, o, m, p,* Ph).

Table 2.8. ^{13}C and ^{29}Si NMR data [a] of starting silanes **22**.

	$\delta^{13}C$ (≡C)	$\delta^{13}C$ (Si-C≡)	$\delta^{13}C$ (=C)	$\delta^{13}C$ (Si-C=)	$\delta^{29}Si$
22a [b]	110.4 [20.4]	78.6 [107.1]	135.2	133.9 [81.2]	-54.6
22c [c]	108.7 [20.0]	87.6 [105.1]	136.7	132.4 [82.1]	-52.7
22e [d]	109.0 [20.3]	87.2 [105.4]	136.4	132.9 [81.8]	-52.8
23a [e]	111.3 [20.3] 108.2 [20.0]	78.2 [108.1], 87.6 [104.3]	135.8	133.4 [81.7]	-53.7

[a] Measured in C_6D_6, coupling constants corresponding to $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$ are given in square brackets; [b] Other ^{13}C data: δ = 30.8, 22.2, 19.9, 13.8 (Bu); [c] Other ^{13}C data: δ = 122.7, 132.4, 129.3, 128.5 (*i, o, p, m,* Ph); [d] Other ^{13}C data: δ = 120.1, 132.4, 125.5, 152.4, 34.7, 31.1 (*i, o, m, p,* $C_{tert.}$, Me, 4-^{t}Bu-C_6H_4); [e] Other ^{13}C data: δ = 13.7, 19.9, 22.1, 30.6 (Bu), 120.1, 132.3, 125.5, 152.3, 34.7, 31.2 (*i, o, m, p,* $C_{tert.}$, Me, 4-^{t}Bu-C_6H_4).

Table 2.9. ^{13}C and ^{29}Si NMR spectroscopic data [a] of silanes **24** and **25**.

	δ ^{13}C (C≡)	δ ^{13}C (Si-C≡)	δ ^{13}C (Si-R^1)	δ ^{29}Si
24a [b]	108.6 [22.7]	80.6 [112.8]	2.4 [67.8]	-67.4
24c [c]	108.5 [22.5]	89.9 [112.7]	3.1 [68.9]	-63.5
25a [d]	110.0 [23.2]	78.4 [116.2]	133.5 [90.3], 134.1, 127.7, 129.9 (*i, o, m, p*)	-71.9
25c [e]	107.7	86.8	132.0, 134.5, 128.2, 130.6 (*i, o, m, p*)	-67.0
25d [f]	108.7 [23.0]	87.3 [116.7]	135.1, 133.0, 128.6, 130.8 (*i, o, m, p*)	-69.1

[a] Measured in C_6D_6, coupling constants are given in square brackets corresponding to $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$; [b] Other ^{13}C data: δ = 30.5, 22.1, 19.8, 13.6 (Bu); [c] data also listed in ref. [34,90]; [d] Other ^{13}C data: δ = 30.2, 21.8, 19.7, 13.4 (Bu); [e] already characterized by IR, GC-MS and NMR (^{13}C, ^1H and ^{29}Si); [89] [f] Other ^{13}C data: δ = 119.7, 132.6, 129.2, 139.5, 21.3 (*i, o, m, p, Me*, 4-Me-C_6H_4).

Table 2.10. Data pertinent to the crystal structure determinations of **24c** and **25c**.

Formula	$C_{25}H_{18}Si$ (**24c**)	$C_{30}H_{20}Si$ (**25c**)
Formula weight	346.48	408.55
Crystal	Prism	Prism
Dimensions [mm]	1.02x0.37x0.29	0.22x0.18x0.14
Crystal system	Trigonal	Triclinic
Space group	R3	P-1
Temperature [K]	133 (2)	293 (2)
Z	3	2
Lattice parameters		
a [pm]	1725.1(2)	634.97(13)
b [pm]	1725.1(2)	1053.1(2)
c [pm]	565.50(10)	2113.3(4)
α [°]	90.00	85.14(3)
β [°]	90.0	88.36(3)
γ [°]	120.00	72.96(3)
Absorption coef. [mm^{-1}]	0.125	0.099
Measuring range [°]	2.4-25.6	1.9-26.1
Volume [$Å^3$]	1457.4(4)	1346.3(5)
Density [Mg/m^3]	1.184	1.008
F(000)	546	428
Goodness-of-fit on F^2	1.06	1.00
Completeness to θ	25.6°:100 %	26.1°:90.7%
Reflections collected	6315	8366
Reflections with $I>2\sigma(I)$	1146	1998
Refined parameters	103	300
Diffractometer	STOE IPDS II	STOE IPDS I
Wave length [pm]	71.069	71.073
wR_2/R_1 [$I>2\sigma(I)$]	0.0292/0.075	0.103/0.354
Max./min. Residual electron density [$epm^{-3}x10^{-6}$]	0.192/-0.180	0.661/-0.223

Table 2.11. ^{13}C and ^{29}Si NMR data [a] of tetraalkyn-1-ylsilanes **26.**

	$\delta^{13}C$ (≡C)	$\delta^{13}C$ (SiC≡)	$\delta^{13}C$ (R)	$\delta^{29}Si$
26b [b]	114.8 [27.3]	80.4 [138.4]	30.4, 28.2	-93.8, -94.4 [e]
26c [c]	106.6 [26.3]	86.0 [129.9]	121.9, 132.5, 128.3, 129.5 (*i, o, m, p*)	n.m.
26d [d]	107.5 [26.1]	86.5 [128.9]	120.2, 133.3, 130.1, 141.0, 21.8 (*i, o, m, p*, *Me*)	-92.7 [e]

[a] Coupling constants corresponding to $^{1}J(^{13}C,^{29}Si)$ and $^{2}J(^{13}C,^{29}Si)$ are given in square brackets; [b] ^{29}Si data taken from ref.; [42] [c] measured in $CDCl_3$; [d] measured in THF-D_8; [e] determined in solid state; n.m. means not measured.

Table 2.12. Crystal data and structure refinement for **26d**.

Formula	$C_{18}H_{14}Si_{0.5}$	Formula weight	244.34
Crystal	Needles	Dimensions [mm]	0.93x0.14x0.14
Crystal system	Tetragonal	Space group	I4(1)/a
Temperature [K]	133 (2)	*Z*	8
Lattice parameters		Absorption coef. [mm^{-1}]	0.105
a [pm]	1966.5 (2)	Measuring range [°]	2.1-25.7
b [pm]	1966.5 (2)	Volume [$Å^3$]	2819.1 (6)
c [pm]	729.0 (11)	Density [Mg/m^3]	1.151
$\alpha = \beta = \gamma$ [°]	90		
Completeness to θ	25.7°:99.2 %	Goodness-of-fit on F^2	1.077
F(000)	1032	Reflections collected	17538
Refined parameters	85	Reflections with $I>2\sigma(I)$	1000
Diffractometer	IPSD STOE II	Wave length [pm]	71.069
wR_2/R_1 [$I>2\sigma(I)$]	0.051/0.112	Max./min. Residual electron density [$epm^{-3}x10^{-6}$]	0.193/-0.272

Table 3.1. ^{11}B, ^{13}C and ^{29}Si NMR data [a] of the alkenes **27 - 30**.

	$\delta^{13}C$ (BC=)	$\delta^{13}C$ (=C)	$\delta^{13}C$ (BEt_2)	$\delta^{11}B$	$\delta^{29}Si$
27c [b]	147.8 (br)	164.1	21.7 (br), 9.4	86.8	-7.7
28a [c]	147.1 (br)	150.5	21.7 (br), 9.0	83.2	12.7
28c [d]	151.4 [72.7, br]	147.5	21.2 (br), 9.0	83.6	12.4
29a [e]	145.6 [74.2, br]	152.5	22.0 (br), 9.1	83.5	-0.4
29a' [f]	144.2 (br)	162.3	20.8 (br), 9.4	83.5	1.4
29b [g]	139.4 [77.2, br]	159.1	21.9 (br), 9.4	82.1	-1.0
29c [h]	148.3 [74.8, br]	149.0	21.6 (br), 9.2	83.6	-1.2
30a [i]	145.1 [88.2, br]	154.9	21.7 (br), 8.9	82.8	-7.8
30a' [j]	n.o. (br)	164.8	n.o. (br), 9.0	82.8	-5.8
30c [k]	147.0 [90.5, br]	151.6	21.3 (br), 8.9	83.0	-8.5
30c' [l]	147.8 (br)	161.1	21.6 (br), 8.9	83.0	-6.9

[a] Measured in C_6D_6, (br) indicates a broad NMR signal owing to partially relaxed ^{11}B-^{13}C scalar coupling, [97,98] n.o. means not observed, some coupling constants $^1J(^{13}C,^{29}Si)$ [± 0.4 Hz] are given in square brackets; [b] Other ^{13}C data: δ = 140.1, 129.5, 128.4, 132.6 (*i, o, m, p,* Ph); [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 8.5 [67.8, Si-Me], 35.5, 31.7, 22.7, 14.2 (Bu); [d] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 7.2 [69.4, Si-Me], 139.3 [6.8], 132.6, 128.6, 128.9 (*i, o, m, p,* Ph); [e] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 36.0, 31.4, 22.6, 14.1 (Bu), 135.1 [91.8], 133.7, 128.6, 131.6, (*i, o, m, p,* Si-Ph); [f] Other ^{13}C data: δ = 36.2, 33.3, 22.2, 13.6 (Bu), 134.7, 133.7, 131.2, 128.4 (*i, o, m, p,* Si-Ph); [g] Other ^{13}C data: δ = 38.0, 29.9 (^{t}Bu), 136.5, 133.6, 131.5, 128.5 (*i, o, m, p,* Si-Ph); [h] Other ^{13}C data: δ = 138.8, 133.6, 133.7, 132.7, 132.1, 128.7, 128.1, 127.8 (Si-Ph, Ph); [i] Other ^{13}C data: δ = 35.5, 31.3, 22.6, 14.3 (Bu); [j] Other ^{13}C data: δ = 33.6, 31.0, 22.5, 14.1 (Bu); [k] Other ^{13}C data: δ = 138.2, 129.6, 128.5, 129.3 (*i, o, m, p,* Ph); [l] Other ^{13}C data: δ = 137.9, 129.6, 128.7, 130.4 (*i, o, m, p,* Ph).

Table 3.2. ^{11}B, ^{13}C and ^{29}Si NMR data [a] of the alkenes **31 - 33.**

	$\delta^{13}C$ (BC=)	$\delta^{13}C$ (=C)	$\delta^{13}C$ (BPr_2)	$\delta^{11}B$	$\delta^{29}Si$
31a [b]	147.6 (br)	151.0	32.8(br), 18.8, 17.6	82.9	13.0
31a´ [c]	145.7 (br)	161.2	32.8(br), 18.9, 17.7	82.9	14.6
31c [d]	152.2 (br)	147.6	32.3(br), 18.8, 17.4	82.8	14.0
31c´ [e]	151.4 (br)	146.7	30.1(br), 18.5, 17.4	82.8	14.3
32a [f]	146.1(br)	152.9	32.9(br), 18.9, 17.7	82.5	-0.2
32a´ [g]	145.2 (br)	151.5	33.4(br), 19.0, 17.8	82.5	1.3
32b [h]	140.1 (br)	159.2	33.0(br), 19.1, 17.8	82.4	-1.0
32b´ [i]	138.9 (br)	159.0	33.0(br), 19.0, 17.7	82.4	-1.1
32c [j]	149.3 [74.8, br]	149.1	32.7(br), 19.0, 17.9	80.2	-1.2
32c´ [k]	148.6 (br)	148.3	32.7(br), 18.6, 17.7	80.2	0.1
33a [l]	145.6 (br)	155.2	32.8 (br), 18.7, 17.6	82.8	-7.4
33c [m]	148.2 (br)	151.5	31.2(br), 18.4, 17.9	83.8	-8.5

[a] Measured in C_6D_6, (br) indicates a broad NMR signal owing to partially relaxed ^{11}B-^{13}C scalar coupling, [97,98] coupling constant for **32c**, $^1J(^{13}C,^{29}Si)$ [± 0.4 Hz] is given in square brackets; [b] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 8.7 [67.6, Si-Me], 35.4, 31.7, 22.7, 14.2 (Bu); [c] Other ^{13}C data: δ = 7.5 (Si-Me), 35.5, 31.7, 22.1, 14.1 (Bu); [d] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 6.2 [70.9, Si-Me], 139.8, 139.8, 132.6, 130.2, 128.6, 128.5, 129.1, 128.9 (Ph groups of **31c** and **31c´**); [e] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 7.2 [69.2, Si-Me]; [f] Other ^{13}C data: δ = 35.9, 31.4, 22.6, 14.1 (Bu), 133.7, 133.6, 132.1, 128.6 (*i, o, m, p,* Si-Ph); [g] Other ^{13}C data: δ = 36.1,31.1, 22.6, 14.0 (Bu), 133.8, 133.6, 128.6, 131.6 (*i, o, m, p,* Si-Ph); [h] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 38.0 [5.1], 30.1 (^{t}Bu), 136.4 [93.7], 133.6, 128.5, 132.8 (*i, o, m, p,* Si-Ph); [i] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 38.2, 30.2 (^{t}Bu); [j,k] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 138.9, 133.6, 132.3, 131.1, 129.1, 128.7, 128.2, 128.1 (Ph, Si-Ph); [l] Other ^{13}C data: δ = 35.5, 31.3, 22.6, 14.1 (Bu); [m] Other ^{13}C data: δ = 137.9, 130.9, 128.7, 130.1 (*i, o, m, p,* Ph).

Table 3.3. ^{11}B, ^{13}C and ^{29}Si NMR data [a] of the alkenes **34 - 36.**

	δ ^{13}C (BC=)	δ ^{13}C (=C)	δ ^{13}C (9-BBN)	δ ^{11}B	δ ^{29}Si
34a [b]	139.2 (br)	166.9	33.9, 33.8, 30.3 (br), 23.1	81.4	-13.6
34a' [c]	143.0 (br)	161.7	33.8, 30.5 (br), 23.2	81.4	-15.1
34c [d]	142.3(br)	159.9	34.5, 34.2, 31.3 (br), 23.4	82.2	- 12.0
35a [e]	144.0 (br)	161.5	33.9, 33.8, 31.2 (br), 31.1	81.6	7.6
35c [f]	148.3 [65.7, br]	156.1	34.7, 34.4, 31.9 (br), 23.5	82.2	7.9
36a [g]	142.9 (br)	163.3	34.2, 31.6 (br), 23.4	81.7	-5.7
36c [h]	144.3 (br)	157.9	34.2, 31.6 (br), 23.1	83.1	-2.1

[a] Measured in $CDCl_3$, (br) indicates a broad NMR signal owing to partially relaxed ^{11}B- ^{13}C scalar coupling; [97,98] [b] Other ^{13}C data: δ [J(^{13}C,^{29}Si)] = 35.3, 31.2, 22.5, 13.9 (Bu), 135.3 [74.1], 134.0, 128.1, 130.3 (*i, o, m, p,* Si-Ph); [c] Other ^{13}C data: δ = 35.1, 31.1, 22.4, 13.9 (Bu), 135.2, 134.0, 128.2, 131.2 (*i, o, m, p,* Si-Ph); [d] Other ^{13}C data: δ [J(^{13}C,^{29}Si)] = 134.2 [76.9], 134.3, 128.1, 129.3 (*i, o, m, p,* Si-Ph), 138.0, 130.2, 129.0, 128.2 (*i, o, m, p*, Ph); [e] Other ^{13}C data: δ [J(^{13}C,^{29}Si)] = 4.2 [58.9, Si-Me], 35.3, 23.1, 22.4, 13.5 (Bu), 137.5 [74.6], 133.5, 127.9, 129.9 (*i, o, m, p,* Si-Ph); [f] measured in C_6D_6; Other ^{13}C data: δ [J(^{13}C,^{29}Si)] = 3.7 [59.8, Si-Me], 133.8 [76.7], 134.0, 129.2, 130.4 (*i, o, m, p*, Si-Ph), 138.0, 130.2, 129.0, 128.2 (*i, o, m, p*, Ph); [g] Other ^{13}C data: δ [J(^{13}C,^{29}Si)] = 35.9, 31.2, 22.6, 13.9 (Bu), 136.0 [77.8], 134.9, 128.3, 130.4 (*i, o, m, p,* $SiPh_2$); [h] Other ^{13}C data: δ [J(^{13}C,^{29}Si)] = 135.4 [78.9], 134.5, 127.8, 128.7 (*i, o, m, p,* $SiPh_2$), 138.3, 130.0, 129.4, 127.5 (Ph).

Table 3.4. ^{11}B, ^{13}C and ^{29}Si NMR data [a] of the alkenes **37 - 40**.

	δ^{13}C (BC=)	δ^{13}C (=C)	δ^{13}C (9-BBN)	δ^{11}B	δ^{29}Si
37c [b]	141.9 [78.5, br]	160.8	34.5, 31.3 (br), 23.6	82.4	-6.4
38a [c]	143.6 [76.2, br]	163.8	34.4, 31.5 (br), 23.4	81.3	16.2
38c [d]	147.6 [76.7, br]	156.7	34.7, 31.8 (br), 23.6	82.9	15.8
39a [e]	141.6 (br)	164.8	34.0, 31.2 (br), 23.0	82.7	3.4
39b [f]	139.5 [80.1, br]	170.9	34.9, 32.4 (br), 23.5	82.3	2.4
39c [g]	143.9 [79.2, br]	158.6	34.3, 31.6 (br), 23.1	83.6	2.2
40a [h]	141.8 (br)	167.0	34.5, 31.6 (br), 23.4	81.5	-3.9
40c [i]	143.0 [95.7, br]	160.8	34.7, 31.9 (br), 23.4	81.3	-4.8

[a] Measured in C_6D_6 at 23 °C, (br) indicates a broad NMR signal owing to partially relaxed ^{13}C-^{11}B scalar coupling; [97,98] some coupling constants $J(^{13}C,^{29}Si)$ [± 0.4 Hz] are given in square brackets; [b] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 138.0 [7.1], 129.6, 128.7, 130.3 (*i, o, m, p,* Ph); [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 9.2 [66.5, Si-Me], 35.3, 31.4, 22.7, 14.1 (Bu); [d] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 8.0 [68.8, Si-Me], 139.5, 129.1, 128.5, 129.6 (*i, o, m, p,* Ph); [e] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 35.3, 30.9, 22.4, 13.9 (Bu), 135.3 [90.7], 133.3, 128.2, 131.2 (*i, o, m, p,* Si-Ph); [f] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 37.8 [4.4], 30.1 (^{t}Bu), 136.6 [92.7], 133.8, 128.5, 131.4 (*i, o, m, p*, Si-Ph); [g] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 132.7, 129.4, 127.9, 125.4 (*i, o, m, p*, Ph), 138.2 [92.7], 133.3, 128.0, 128.2 (*i, o, m, p,* Si-Ph); [h] Other ^{13}C data: δ = 35.4, 31.1, 22.8, 14.1 (Bu); [i] Other ^{13}C data: δ = 128.4, 130.4, 129.8, 138.0 (*i, o, m, p*, Ph).

Table 3.5. Coupling constants [a] and their difference for conversion of -C≡C- (alkyn-1-ysilanes) to -C=C- (alkenylsilanes).

Alkyn-1-ylsilane	$^{1}J(^{13}C,^{29}Si)$/Hz	Alkenylsilane	$^{1}J(^{13}C,^{29}Si)$/Hz	Difference/Hz
2c	107.8	**35c**	65.7	42.1
4c	134.2	**37c**	78.5	55.7
5a	133.8	**38a**	76.2	57.6
5c	131.3	**38c**	76.7	54.6
6b	138.9	**39b**	80.1	58.8
6c	139.9	**39c**	79.2	60.7
7c	175.4	**40c**	95.7	79.7

[a] Summary of Table 2.1, Table 2.2, Table 3.3 and Table 3.4. For all the compounds it was not possible as $^{1}J(^{13}C(B),^{29}Si)$ can be determined from ^{29}Si NMR spectra. It requires sufficiently long time to record ^{29}Si NMR spectra with appropriate signal-to-noise ratio in order to get ^{13}C satellites.

Table 3.6. Selected bond lengths (pm) and angles (deg.) of alkenylsilanes **35c**, **37c** and **39c**.

$C_{23}H_{28}BClSi$ (**35c**)		$C_{16}H_{20}BCl_2Si$ (**37c**)		$C_{22}H_{25}BCl_2Si$ (**39c**)	
C17-Si	186.0(8)	H-Si	119.9	C1–Si1	185.2(2)
C9-C10	135.9(9)	C9-C10	134.8(4)	C7–C8	135.0(3)
C9-B	153.9(11)	C9-B	156.9(5)	C7–B1	156.1(3)
C9-Si	184.1(8)	C9-Si	185.1(3)	C7–Si1	184.2(2)
C10-C11	146.8(10)	C10-C11	147.8(4)	C8-C9	1.471(3)
Si–Cl	207.2(3)	Si–Cl1	203.70(17)	Si1–Cl1	204.86(9)
Si-C23	183.3(6)	Si1-Cl2	206.20(16)	Si1–Cl2	205.60(8)
C10-C9-B	115.4(7)	C10-C9-B	117.4(3)	C8–C7–B1	116.5(2)
C10-C9-Si	125.2(6)	C10-C9-Si	122.4(2)	C8–C7–Si1	127.5(2)
B-C9-Si	119.4(6)	B-C9-Si	120.1(2)	B1–C7–Si1	115.9(2)
C9-C10-C11	132.3(8)	C9-C10-C11	130.5(3)	C7–C8–C9	130.7(2)
C1-B-C5	109.8(7)	C1-B-C5	110.5(3)	C22–B1–C15	111.4(2)
C1-B-C9	127.9(8)	C1-B-C9	125.4(3)	C7–B1–C15	122.9(2)
C5-B-C9	121.7(8)	C5-B-C9	124.0(3)	C7–B1–C22	125.1(2)
--	--	--	--	C7–Si1–C1	108.7(1)
C9-Si-Cl	110.8(3)	C9-Si-Cl1	113.76(12)	C7–Si1–Cl1	114.39(8)
C9-Si-C23	115.9(3)	C9-Si-Cl2	107.60(11)	C7–Si1–Cl2	111.92(8)
C17-Si-C23	108.8(4)	Cl1-Si-Cl2	106.30(7)	Cl1–Si1–Cl2	106.38(4)

Table 3.7. Data relevant to the crystal structure determination of **35c**, **37c** and **39c.**

Formula	$C_{23}H_{28}BClSi$ (**35c**)	$C_{16}H_{20}BCl_2Si$ (**37c**)	$C_{22}H_{25}BCl_2Si$ (**39c**)
Formula weight	378.80	322.12	399.22
Crystal	Prism	Prism	Needle
Dimensions [mm]	0.16x0.14x0.12	0.22x0.15x0.12	0.87x0.32x0.28
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2(1)/c	P-1	P2(1)/n
Temperature [K]	293 (2)	293 (2)	191 (2)
Z	4	2	4
Lattice parameters			
a [pm]	1580.1(3)	751.30(15)	655.00(4)
b [pm]	649.06(13)	975.5(2)	2297.90(16)
c [pm]	2090.0(4)	1250.8(3)	1383.60(10)
α [°]	90.00	92.44(3)	90.00
β [°]	91.25(3)	98.85(3)	95.305(5)
γ [°]	90.00	110.66(3)	90.00
Absorption coef. [mm^{-1}]	0.238	0.443	0.374
Measuring range [°]	2.0-26.2	2.2-26.1	1.7-25.7
Volume [$Å^3$]	2143.0 (7)	842.9 (3)	2073.6(2)
Density [Mg/m^3]	1.174	1.269	1.279
F(000)	808	338	840
Goodness-of-fit on F^2	0.498	0.820	1.001
Completeness to θ	26.2°:96.7 %	26.1°:91.0	25.7°:99.5
Reflections collected	14282	5126	26069
Reflections with $I>2\sigma(I)$	562	1628	3096
Refined parameters	235	182	239
Diffractometer	IPSD STOE I	IPSD STOE I	IPSD STOE II
Wave length [pm]	71.073	71.073	71.069
wR_2/R_1 [$I>2\sigma(I)$]	0.0467/0.139	0.0544/0.1525	0.0487/0.135
Max./min. residual electron density [$epm^{-3}x10^{-6}$]	0.138/-0.104	0.433/-0.246	0.858/-0.319

Table 3.8. ^{11}B, ^{13}C and ^{29}Si NMR data [a] of alkenyl(dichloro)vinylsilanes **41**, **42**.

	41a [b]	**41c** [c]	**42c** [d]
$\delta^{13}C$ (BC=)	145.4 (br)	149.5 [74.1, br]	150.9 (br)
$\delta^{13}C$ (=C)	151.9	148.4	148.4
$\delta^{13}C$ (R)	35.8, 31.6, 22.6, 14.2	139.7, 136.8, 128.4, 130.4 (*i, o, m, p*)	139.9, 129.2, 128.4, 128.9 (*i, o, m, p*)
$\delta^{13}C$ (BEt_2 / BPr_2)	21.7 (br), 9.0	21.4 (br), 9.0	29.2 (br), 18.3, 17.7
$\delta^{11}B$	83.0	84.2	81.2
$\delta^{29}Si$	-2.0	-2.5	-8.4

[a] Measured in C_6D_6, coupling constants $J(^{13}C,^{29}Si)$ in Hz are given in brackets [± 0.4 Hz], (br) denotes a broad ^{13}C resonance signal as the result of partially relaxed scalar ^{11}B-^{13}C coupling; [97,98] [b] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 134.9 [88.9, Si-CH=], 136.7 (=CH_2); [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 132.7 [89.7, Si-CH=], 138.6 (=CH_2); [d] Other ^{13}C data: δ = 132.2 (Si-CH=), 136.3 (=CH_2).

Table 3.9. ^{11}B, ^{13}C and ^{29}Si NMR data [a] of 1, 2-hydroboration products **43** - **48** of vinylsilanes.

	$\delta^{13}C$ (Si-C)	$\delta^{13}C$ (CH_2-B)	$\delta^{13}C$ (BR_2)	$\delta^{13}C$ (Me)	$\delta^{29}Si$	$\delta^{11}B$
43 [b]	29.8 (br)	--	19.4 (br), 8.2	10.0	29.2	86.2
43´ [c]	15.3	18.2 (br)	19.4 (br), 8.3	--	34.3	86.2
44 [d]	30.3 (br)	--	31.2 (br), 18.4, 17.8	10.0	29.0	86.0
44´ [e]	15.5 [69.1]	23.9 (br)	30.7 (br), 18.1, 17.7	--	34.2	86.0
45 [f]	15.4 [69.6]	18.8 (br)	33.5, 31.3 (br), 23.5	--	34.4	87.5
46	31.2 (br)	--	19.9 (br), 8.2	10.0	9.1	86.0
46´	18.5	19.5 (br)	20.5 (br), 8.1	--	14.8	86.0
47	31.8 (br)	--	30.6 (br), 18.2, 17.6	9.9	9.1	86.1
48	18.7 [85.7]	19,0 (br)	33.5, 31.3 (br), 23.5	--	14.7	87.4

[a] Measured in C_6D_6 at 23 °C, (br) indicates a broad NMR signal owing to partially relaxed ^{11}B-^{13}C scalar coupling; [97,98] some coupling constants $^1J(^{13}C,^{29}Si)$ in Hz are given in square brackets (± 0.4 Hz); [b] Other ^{13}C data: δ = 5.4 (Si-Me); [c] Other ^{13}C

data: δ = 4.2 (Si-Me); [d] Other ^{13}C data: δ = 4.3 (Si-Me); [e] Other ^{13}C data: δ [J(^{13}C,^{29}Si)] = 4.4 [66.5, Si-Me]; [f] Other ^{13}C data: δ [J(^{13}C,^{29}Si)] = 4.5 [66.4, Si-Me].

Table 3.10. ^{11}B, ^{13}C and ^{29}Si NMR data [a] of the di(alkenyl)silanes **49a**, **50a** and alkyn-1-ylborates **55a**, **56c**.

	δ ^{13}C (BC=)	δ ^{13}C (=C)	δ ^{13}C (9-BBN)	δ ^{13}C (R)	δ ^{11}B	δ ^{29}Si
49a [b]	148.3 (br)	158.3	34.5, 31.4 (br), 23.7	35.7, 33.8, 31.7, 14.3.	81.9	4.2
50a	146.4 (br)	161.5	34.5, 31.4 (br), 23.6	35.7, 33.8, 31.4, 14.2	81.7	0.5
55a [c]	143.4 (br)	163.2	34.3, 31.6 (br), 23.4	35.9, 31.2, 22.6, 13.9	-16.5	-16.0
56c [d]	151.2 **(**br**)**	155.8	34.7, 34.6, 31.9 (br), 23.7	Ph carbons not assigned	-16.8	11.2, -17.6

[a] Measured in C_6D_6, coupling constants J(^{13}C,^{29}Si) [± 0.4 Hz] are given in square brackets; (br) denotes a broad ^{13}C resonance signal as the result of partially relaxed scalar ^{13}C–^{11}B spin-spin coupling; [97,98] [b] Other ^{13}C data: δ [J(^{13}C,^{29}Si)] = 6.8 [56.4, Si-Me]; [c] Other ^{13}C data: δ = 89.1 (≡C-), ≈ 103 (B-C≡, broad signal not observed), 136.2, 135.1, 128.9, 130.5 (*i, o, m, p,* Si-Ph, other carbons are with out assignment); [d] Other ^{13}C data: δ [J(^{13}C,^{29}Si)] = -1.2 [54.9, $SiMe_3$], 0.8 [57.3, Si-Me], 107.9 [91.5, ≡C-$SiMe_3$], 106.2 (br, B-C≡), 138.2 [73.7, *i*], 140.5 [4.5, *i*] other carbons are with out assignment.

Table 3.11. ^{11}B, ^{13}C and ^{29}Si NMR data [a] of the alkenyl(alkyn-1-yl)silanes **51 - 54**

	δ^{13}C (BC=)	δ^{13}C (=C)	δ^{13}C (Si-C≡)	δ^{13}C (≡C)	δ^{11}B	δ^{29}Si
51a [b]	143.9 (br)	161.8	82.8 [95.7]	111.2 [17.2]	83.5	-36.8
52a [c]	144.0 [73.4, br]	162.2	82.9 [104.9]	110.7 [21.1]	81.9	-15.6
52c [d]	147.7 [73.7, br]	156.3	91.8 [103.9]	108.2 [20.5]	83.6	-14.6
53c [e]	144.1 [75.5, br]	158.7	90.2 [109.0]	109.3 [21.3]	84.6	-23.7
54a [f]	141.8 (br)	165.8	81.3 [132.1]	112.5 [26.9]	81.7	-24.4

[a] Measured in C_6D_6, coupling constants $J(^{13}C,^{29}Si)$ [± 0.4 Hz] are given in square brackets, (br) denotes a broad ^{13}C resonance signal as the result of partially relaxed scalar ^{11}B-^{13}C spin-spin coupling; [97,98] [b] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 35.9, 33.8, 22.9, 14.1 (=C-Bu), 31.5, 22.2, 20.1, 13.7 (≡C-Bu), 34.3, 31.5 (br), 23.6 (9-BBN),137.1 [74.5], 135.6, 128.2, 129.6 (*i, o, m, p,* $SiPh_2$); [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 6.2 [64.6, Si-Me], 35.2, 31.7, 22.2, 14.3 (=C-Bu), 30.5, 22.9, 19.9, 13.7 (≡C-Bu), 34.4, 34.5, 31.3 (br), 23.6 (9-BBN); [d] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 5.1 [65.9, Si-Me], 34.7, 34.7, 31.7(br), 23.7 (9-BBN), 140.0, 132.5, 129.9, 129.5, 129.4, 128.6, 128.5, 122.5 (Ph); [e] Other ^{13}C data: δ = 34.7, 34.6, 31.9 (br), 23.6 (9-BBN), 139.1, 135.5, 134.5, 134.3, 132.6, 132.4, 130.7, 130.3, 129.4, 129.0, 128.7, 122.3 (Ph, Si-Ph); [f] Other ^{13}C data: δ = 35.2, 31.3, 29.9, 22.8, 22.1, 19.7, 13.6, 14.2 (Bu), 34.5, 31.7 (br), 23.5 (9-BBN).

Table 3.12. ^{11}B, ^{13}C and ^{29}Si NMR data [a] of alkenyl(alkyn-1-yl)silanes **57 - 61**

	δ^{13}C (BC=)	δ^{13}C (=C)	δ^{13}C (Si-C≡)	δ^{13}C (≡C)	δ^{29}Si	δ^{11}B
57a [b]	141.2 (br)	161.3	94.0 [87.8]	107.8 [16.9]	-32.6	81.6
57c [c]	147.8 (br)	155.7	93.7 [88.8]	108.4 [16.5]	-31.8	82.4
58 [d]	142.9 (br)	162.6	92.7 [91.5]	108.6 [n.m.]	-35.7	83.1
58c [e]	145.0 (br)	158.0	92.1 [n.m.]	109.1 [n.m.]	-35.3	83.6
59c [f]	141.6 (br)	159.4	109.4 [83.8] [12.4]	118.7 [76.3] [12.7]	-18.7, -51.8	82.4
60a [g]	143.9 (br)	161.5	113.5 [81.1] [12.4]	116.1 [77.5] [12.0]	-19.4, -34.1	80.9
60c [h]	147.7 (br)	154.1	113.2 [81.9] [12.3]	116.9 [77.1] [12.4]	-19.2, -33.1	82.9
61a [i]	142.8 (br)	162.8	112.3 [84.3] [11.4]	118.0 [76.7] [12.3]	-18.6, -37.3	81.2
61c [j]	144.8 (br)	158.0	111.2 [86.1] [12.6]	118.1 [76.8] [12.8]	-18.9, -36.6	82.2

[a] Measured in C_6D_6 at 23 °C, coupling constants $J(^{13}C,^{29}Si)$ [± 0.4 Hz] are given in square brackets, n.m. means not measured, (br) denotes a broad ^{13}C resonance signal as the result of partially relaxed scalar ^{11}B-^{13}C spin-spin coupling; [97,98] [b] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 0.8 [58.6, Si-Me], 34.7, 34.6, 31.8 (br), 23.7 (9-BBN), 35.1, 27.2, 23.0, 14.4 (Bu), 138.5 [74.0], 134.8, 128.1, 129.6 (*i, o, m, p,* Si-Ph), 123.7, 132.2, 128.4, 140.5 (*i, o, m, p,* Ph); [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 0.1 [58.3, Si-Me], 34.4, 34.4, 31.4 (br), 23.6 (9-BBN), 138.2 [71.9], 134.6, 129.6, 129.8 (*i, o, m, p,* Si-Ph), 123.2, 134.6, 132.3, 132.2, (*i, o, m, p,* Ph); [d] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 34.3, 31.4 (br), 23.5 (9-BBN), 36.0, 31.4, 22.7, 14.0 (Bu), 136.4 [74.9], 135.7, 128.4, 129.8, (*i, o, m, p,* $SiPh_2$); [e] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 34.5, 32.1 (br), 23.6 (9-BBN), 136.5 [76.0], 135.7, 128.4, 129.7 (*i, o, m, p,* $SiPh_2$), 139.6, 137.9, 132.6, 132.4, 128.5, 127.9, 125.7, 123.6 (Ph); [f] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = -0.3 [55.9, $SiMe_3$], 34.5, 34.3, 31.2 (br), 23.7 (9-BBN), 134.2 [74.9], 135.3, 130.0, 128.4 (*i, o, m, p,* Si-Ph), 128.2, 129.9, 129.2, 139.5 (*i, o, m, p,* Ph); [g] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = -0.2 [56.3, $SiMe_3$], 1.0 [56.5, Si-Me], 34.4, 31.3 (br), 23.7 (9-BBN), 35.6, 31.7, 22.9, 14.3 (Bu), 138.0 [72.8], 134.6, 129.6, 128.3 (*i, o, m, p,* Si-Ph); [h] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = -0.003 [55.6, $SiMe_3$], -0.2 [56.4, Si-Me], 34.5, 34.6, 31.7 (br), 23.7 (9-

BBN), 140.7 [64.9], 141.4 [4.2] other carbons are with out assignment; [i] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = –0.2 [56.4, $SiMe_3$], 34.3, 31.4 (br), 23.6 (9-BBN), 36.0, 27.2, 22.8, 14.1 (Bu), 136.2 [72.6], 135.6, 129.8, 129.3 (*i, o, m, p,* $SiPh_2$); [j] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = -0.2 [56.4, $SiMe_3$], 34.5, 31.9 (br), 23.6 (9-BBN), 136.3 [75.6], 135.6, 130.4, 128.2 (*i, o, m, p,* $SiPh_2$), 125.7, 135.4, 129.7, 139.5, (*i, o, m, p,* Ph).

Table 3.13. ^{11}B, ^{13}C and ^{29}Si NMR data [a] of alkenyl(dialkyn-1-yl)silanes **62 - 67**.

	$\delta^{13}C$ (BC=)	$\delta^{13}C$ (C=)	$\delta^{13}C$ (Si-C≡)	$\delta^{13}C$ (≡C)	$\delta^{29}Si$	$\delta^{11}B$
62a [b]	144.2 [70.4, br]	160.4	83.3 [99.5]	108.6 [19.5]	-54.1	82.3
62c [c]	146.5 [70.1, br]	155.7	92.4 [98.6]	107.5 [18.6]	-51.1	86.4
63a [d]	141.2 (br)	164.1	91.2 [101.2]	108.3 [18.8]	-55.8	82.7
63c [e]	143.8 (br)	158.1	90.8 [102.8]	108.7 [20.0]	-55.2	84.3
63d[f]	152.8 [82.8, br]	158.3	90.3 [102.9]	108.8 [19.5]	-55.2	84.5
65c [g]	144.2 [83.1, br]	150.1	87.8 [104.6]	108.9 [19.2]	-61.4	85.6
66a [h]	148.1 (br)	157.4	85.8	108.8	-41.1	82.7
66c [i]	149.5 (br)	151.7	96.3 [85.5]	108.8 [15.8]	-39.4	86.4
67c [j]	143.9 (br)	158.7	89.3 [86.2]	108.6 [16.3]	-29.1	84.0

[a] Measured in C_6D_6, coupling constants $J(^{13}C,^{29}Si)$ [± 0.4 Hz] are given in square brackets, (br) denotes a broad ^{13}C resonance signal; [97,98] [b] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 2.9 [60.6, Si-Me], 34.4, 31.1 (br), 23.7 (9-BBN), 35.1, 31.1, 23.0, 14.3 (=C-Bu), 30.7, 22.2, 20.0, 13.7 (C≡C-Bu); [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 2.0 [63.0, Si-Me], 35.1, 31.8 (br), 23.8 (9-BBN), Ph carbons without assignment; [d] Other ^{13}C data: δ = 34.5, 31.6 (br), 23.7 (9-BBN), Bu carbons without assignment; [e] Other ^{13}C data: δ = 34.6, 31.8 (br), 23.6 (9-BBN), 139.7 [4.8, *i*], 135.8 [83.2, *i*], 135.3, 132.4, 129.0, 128.5, 128.4, 128.1 (Ph, Si-Ph) 123.2, 132.5, 128.3, 130.6 (*i, o, m, p,* ≡C-Ph); [f] Other ^{13}C data: δ = 34.7, 31.8 (br), 23.7 (9-BBN), 21.3, 21.3 (Me, Me, 4-Me-C_6H_4) other carbons are not assigned, Si-Ph and 4-Me-C_6H_4; [g] other NMR data not assigned; [h] Other ^{13}C data: δ = 3.3 (Si-Me), 34.4, 31.4 (br), 23.8 (9-BBN), 35.5, 31.9, 23.1, 14.3 (C=C-Bu), 30.9, 22.2, 19.8, 13.7 (C≡C-Bu); [i] Other ^{13}C data. δ [$J(^{13}C,^{29}Si)$]= 4.2 [56.8, Si-Me], 34.8, 31.9 (br), 23.8 (9-BBN); [j] Other ^{13}C data: δ = 34.7, 32.0 (br), 23.5 (9-BBN).

Table 3.14. ^{11}B ^{13}C and ^{29}Si NMR data [a] of the dialkenyl(dialkyn-1-yl)silane derivatives **68b - d**.

	$\delta^{13}C$ (BC=)	$\delta^{13}C$ (=C)	$\delta^{13}C$ (Si–C≡)	$\delta^{13}C$ (≡C)	$\delta^{29}Si$	$\delta^{11}B$
68b [b]	146.1 [72.4, br]	161.4	84.1 [100.6]	118.1 [18.3]	-65.7	82.7
68c [c]	146.1 (br)	153.5	93.3 [99.1]	109.8 [19.3]	-62.8	84.3
68d [d]	145.3 [71.2, br]	153.7	92.9 [99.5]	109.3 [18.9]	-62.9	85.0

[a] Measured in C_6D_6, coupling constants $J(^{13}C,^{29}Si)$ [± 0.3 Hz] are given in square brackets, (br) denotes a broad ^{13}C resonance signal as the result of partially relaxed scalar ^{11}B-^{13}C spin-spin coupling; [97,98] [b] Other ^{13}C data: δ = 35.1, 31.8 (br), 23.9 (9-BBN), 37.7, 30.8, 30.5, 28.5 (*t*Bu); [c] Other ^{13}C data: δ = 34.8, 31.9 (br), 23.8 (9-BBN), 140.1, 137.9, 132.5, 132.2, 130.8, 129.3, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 127.8, 125.7, 123.7 (Ph); [d] Other ^{13}C data: δ = 34.8, 34.4, 31.8 (br), 23.8 (9-BBN), 21.4, 21.3, 138.8, 138.4, 137.6, 132.4, 132.1, 131.0, 129.3, 129.1, 128.5, 120.9 (4-Me-C_6H_4).

Table 4.1. ^{11}B, ^{13}C and ^{29}Si NMR data [a] of the 1-silacyclobutenes **69 - 73** and **77** for comparison.

	δ ^{13}C (=CH)	δ ^{13}C (C2)	δ ^{13}C (C3)	δ ^{13}C (C4)	δ ^{29}Si	δ ^{11}B
69c [b]	n.a.	141.9 [n.o.]	173.3 (br)	159.4 [n.o.]	-16.4	86.7
70c [c]	130.1	147.2 [58.0]	179.9 (br)	157.2 [63.8]	10.7	85.7
71c [d]	134.4	146.2 [58.8]	182.8 (br)	156.3 [63.6]	-1.2	86.9
72a [e]	129.3	147.8 [67.5]	179.4 (br)	158.3 [70.0]	-8.1	87.5
73a [f]	130.5 [12.3]	148.1 [67.2]	179.5 (br)	158.4 [69.3]	-10.7	86.8
77a [g]	131.1 [11.8]	148.0 [66.5]	176.5 (br)	163.1 [67.9]	-9.2	86.3

[a] Measured in C_6D_6, coupling constants $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$ are given in square brackets [± 0.4 Hz], (br) denotes a broad ^{13}C resonance signal as the result of partially relaxed scalar ^{11}B-^{13}C coupling; [97,98] [b] Other carbons were not assigned, as silole accompanied by some other unknown side products are present; [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 3.6 [52.0, Si-Me], 21.6 (br), 9.0 (BEt_2), 139.0, 137.3, 129.3, 129.1, 128.9, 128.1, 127.9 (Ph); [d] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 21.7 (br), 9.3 (BEt_2), 138.4 [4.6], 136.9 [5.3], 134.3, 132.7, 132.5, 130.3, 129.3, 128.9, 128.9, 128.2, 128.0, 127.1 (Si-Ph, Ph); [e] Other ^{13}C data: δ = 21.7 (br), 9.3 (BEt_2), 34.2, 32.3, 31.7, 30.7, 22.9, 22.7, 14.2, 13.1 (Bu); [f] Other ^{13}C data: δ = 32.8 (br), 18.5, 17.7 (BPr_2), 34.3, 32.4, 31.8, 30.7, 23.0, 22.6, 14.2, 14.0 (Bu); [g] Other ^{13}C data: δ = 33.3, 31.5 (br), 23.2 (9-BBN), 34.5, 32.5, 31.9, 31.1, 23.0, 22.7, 14.2, 14.1 (Bu).

Table 4.2. ^{11}B, ^{13}C, ^{29}Si NMR data[a] of the silacyclobutenes **74 - 76, 78 - 81**.

	δ ^{13}C (HC=)	δ ^{13}C (C-2)	δ ^{13}C (C-3)	δ ^{13}C (C-4)	δ ^{29}Si	δ ^{11}B
74a [b]	135.6	146.0 [54.9]	178.6(br)	166.9 [53.4]	-0.3	86.7
75a [c]	128.9 [12.2]	147.1 [58.4]	175.9 (br)	165.3 [58.7]	11.7	84.2
75c [d]	131.0	147.8 [57.9]	177.8 (br)	161.0 [61.1]	11.0	86.8
76c [e]	132.6	146.9 [58.8]	180.6 (br)	160.2 [62.4]	-1.8	84.6
78c [f]	140.0	147.6 [54.3]	180.4(br)	162.5 [55.4]	-10.5	85.0
79a [g]	140.1	147.0 [55.1]	177.9 (br)	159.8 [54.9]	3.2	87.2
79c [h]	140.8	148.8 [53.0]	178.7 (br)	163.3 [55.2]	-11.6	86.0
80a [i]	140.0	146.4 [n.o.]	163.4 (br)	158.8 [n.o.]	-2.0	89.1
80c [j]	139.6	147.6 [53.0]	180.4 (br)	162.5 [55.8]	-1.4	89.6
81c [k]	139.8	151.7 [48.7] [15.1]	194.9 (br)	166.8 [38.2] [63.3]	-11.6, -12.9	88.2

[a] Measured in C_6D_6 at 23 °C, coupling constants $J(^{13}C,^{29}Si)$ are given in square brackets [± 0.4 Hz], n.o. means not observed, (br) denotes a broad ^{13}C resonance signal as the result of partially relaxed scalar ^{11}B-^{13}C coupling; [97,98] [b] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 33.4, 31.9 (br), 23.5 (9-BBN), 35.1, 34.4, 33.1, 32.6, 23.1, 22.7, 14.2, 14.0 (Bu), 135.5 [62.7], 135.7, 130.2, 128.4, (*i, o, m, p,* $SiPh_2$); [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 3.4 [49.8, Si-Me]. 34.4, 34.2, 32.2 (br), 23.4 (9-BBN), other carbons are without assignment; [d] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 3.2 [51.8, Si-Me], 34.4, 34.2, 32.2 (br), 23.4 (9-BBN), 139.1 [5.3], 137.7 [4.6], 131.1, 129.8, 129.1, 128.9, 128.1, 127.8, (Ph); [e] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 34.5, 34.3, 32.4 (br), 23.5 (9-BBN), 138.7 [5.3], 137.5 [4.6], 132.7 [71.1], 134.5, 131.8, 131.3, 130.0, 129.0, 128.9, 128.9, 128.6, 128.5 (Si-Ph, Ph); [f] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 34.4, 32.4 (br), 23.5 (9-BBN), 134.2 [64.8], 135.9, 128.7, 130.6 (*i, o, m, p,* Si-Ph), 135.5, 132.6, 130.7, 128.8, 128.5, 128.4, 127.6, 127.2 (Ph); [g] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = -3.1 [64.8, Si-Me], 34.2, 31.1 (br), 23.6 (9-BBN), 35.0, 32.6, 22.7, 14.2 (Bu),136.5 [62.8], 134.6, 128.5, 130.5 (*i, o, m, p,* Si-Ph), 132.5, 128.6, 128.3, 127.1 (*i, o, m, p,* Ph); [h] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = -1.3 [52.3, Si-Me], 34.7, 32.4 (br), 23.6 (9-BBN), 140.7 [65.1], 134.6, 128.3, 129.1 (*i, o, m, p,* Si-Ph), 132.5, 132.3, 128.8, 128.5, 128.2, 128.1, 127.1, 126.8 (Ph); [i] Other ^{13}C data: δ = 34.3, 32.3 (br), 23.6 (9-BBN), 35.4, 32.5, 22.7, 14.1 (Bu), 139.9, 135.8, 128.6, 130.6 (*i, o, m, p,* $SiPh_2$), 135.1, 130.7, 128.7, 127.4 (*i, o, m, p,* Ph); [j] Other ^{13}C data: δ = 34.4, 32.4 (br), 23.6 (9-BBN), 139.6, 136.0, 128.8,

130.7, (*i, o, m, p,* $SiPh_2$), 135.5, 134.2, 132.7, 130.6, 128.9, 128.6, 127.4, 127.2 (Ph); [k] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = -2.1 ($SiMe_3$), 0.3 (Si-Me), 33.8, 33.7, 32.4 (br), 23.5 (9-BBN), Ph and Si-Ph carbons are with out assignment.

Table 4.3. Crystal data and structure refinement for **80a**.

Formula	$C_{34}H_{39}BSi$	Formula weight	486.55
Crystal	Prism	Dimensions [mm]	0.7x0.46x0.2
Crystal system	Triclinic	Space group	P-1
Temperature [K]	191 (2)	*Z*	2
Lattice parameters		Absorption coef. [mm^{-1}]	0.103
a [pm]	996.70 (8)	Measuring range [°]	2.2-25.1
b [pm]	1168.40 (9)	Volume [$Å^3$]	1415.8(2)
c [pm]	1351.60 (11)	Density [Mg/m^3]	1.141
α [°]	76.073 (6)	Completeness to θ	25.1°:99.1 %
β [°]	88.097 (7)	Goodness-of-fit on F^2	1.047
γ [°]	68.209 (6)		
F(000)	524	Reflections collected	17682
Refined parameters	329	Reflections with $I>2\sigma(I)$	4297
Diffractometer	STOE IPDS II	Wave length [pm]	71.069
wR_2/R_1 [$I>2\sigma(I)$]	0.0426/0.104	Max./min. Residual electron density [$epm^{-3}x10^{-6}$]	0.319 /-0.244

Table 4.4. ^{11}B, ^{13}C and ^{29}Si NMR data [a] for 1-silacyclobuten derivatives **82 - 86**.

	δ ^{13}C (C-2)	δ ^{13}C (C-3)	δ ^{13}C (C-4)	δ ^{13}C (C=)	δ ^{29}Si	δ ^{11}B
82c [b]	147.2 [57.3]	177.4 (br)	161.4 [59.4]	132.4	-18.1	88.2
83c [c]	146.0 [58.3]	181.6(br)	160.2 [60.0]	138.9	-23.5	85.8
83d [d]	145.4 [58.2]	180.7 (br)	160.1 [60.2]	139.6	-24.0	87.9
84c [e]	146.0 [56.5]	179.5 (br)	170.1 [59.6]	n.a.	-24.8	87.3
85c [f]	151.3 [52.7]	178.8 (br)	168.2 [52.1]	137.8	-1.6	88.2
86c [g]	150.7 [n.o.]	180.4(br)	164.9 [n.o.]	139.8	-11.2	85.8

[a] Measured in C_6D_6 at 23 °C, some coupling constants $^1J(^{13}C,^{29}Si)$ are given in square brackets, n.o. means not observed due to low concentration, (br) denotes a broad ^{13}C resonance signal as a result of partially relaxed scalar ^{11}B-^{13}C coupling, [97,98] Ph group carbons are without assignment; [b] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 0.07 [53.0, Si-Me], 34.0, 34.1, 31.9 (br), 23.7 (9-BBN), 90.7 [82.7, Si-C≡], 110.2 [16.0, ≡C]; [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 34.4, 32.3 (br), 23.5 (9-BBN), 88.2 [86.6, Si-C≡], 111.6 [16.3, ≡C]; [d] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 34.4, 34.4, 32.2 (br), 23.6 (9-BBN), 88.1 [86.4, Si-C≡], 112.1 [16.4, ≡C], 21.4, 21.2 (Me, 4-Me-C_6H_4) other carbons are without assignment; [e] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 36.0 [4.3], 30.9, 30.6, 28.7 (^{t}Bu), 21.9 (br), 9.6 (BEt_2), 78.3 [86.7, Si-C≡], 120.7 [15.9, ≡C], 139.8 [70.9, *i*]; [f] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = -0.01 [47.8, Si-Me], 33.8, 33.9, 34.1, 34.2, 31.9 (br), 32.0 (br), 23.5, 23.7 (9-BBN), 153.8 (=C), 150.1 (br, BC=); [g] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 33.9, 33.9, 32.2 (br), 23.8, 23.6 (9-BBN), 157.1 (=C), 146.5 (br, BC=).

Table 4.5. ^{11}B, ^{13}C and ^{29}Si NMR data [a] of the 4-silaspiro[3.3]hepta-1,5-diene derivatives **88b - d**.

	δ^{13}C (C-1,5)	δ^{13}C (C-2,6)	δ^{13}C (C-3,7)	δ^{13}C (=CH)	δ^{29}Si	δ^{11}B
88b [b]	171.4 [49.3]	178.0 (br)	144.6 [47.4]	141.4 [12.1]	-2.4	87.1
88c [c]	163.7 [49.2]	181.3 (br)	148.8 [48.3]	139.8	-0.9	88.0
88d [d]	163.2 [49.4]	180.0 (br)	148.0 [48.1]	132.3	-0.9	87.4

[a] Measured in C_6D_6, (br) indicates a broad NMR signal owing to partially relaxed ^{11}B-^{13}C scalar coupling; [97,98] Coupling constants $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$ are given in square brackets; [b] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 34.41, 34.37, 32.5 (br), 23.7 (9-BBN), 35.8 [4.1], 35.1 [5.2], 32.3, 29.9 (^{t}Bu); [c] Other ^{13}C data: δ = 34.4, 34.2, 32.4 (br), 23.5 (9-BBN), 139.2, 129.3, 128.7, 132.8, 127.3, 128.3, 127.6, 128.8, (Ph); [d] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 34.5, 34.3, 32.4(br), 23.7 (9-BBN), 137.3 [4.2, *i*] 136.6 [4.7, *i*], 129.6, 129.5, 128.5, 127.3, 137.5 (*p*), 137.0 (*p*), 21.2, 21.1 (Me) (4-Me-C_6H_4).

Table 4.6. Data for Crystal structure determination of **88d**.

Formula	$C_{52}H_{58}B_2Si$	Formula weight	732.69
Crystal	Prism	Dimensions [mm]	0.27x0.25x0.23
Crystal system	Monoclinic	Space group	P2(1)/c
Temperature [K]	273(2)	*Z*	4
Lattice parameters		Absorption coef. [mm^{-1}]	0.090
a [pm]	1842.5(3)	Measuring range [°]	2.0-25.7
b [pm]	1961.0(2)	Volume [$Å^3$]	4233.6(8)
c [pm]	1173.18(11)	Density [Mg/m^3]	1.150
α [°]	90.00	Completeness to θ	25.7°:47.0 %
β [°]	92.863(10)	Goodness-of-fit on F^2	0.885
γ [°]	90.00		
F(000)	1576	Reflections collected	15719
Refined parameters	496	Reflections with $I>2\sigma(I)$	1505
Diffractometer	STOE IPDS II	Wave length [pm]	71.069
wR_2/R_1 [$I>2\sigma(I)$]	0.062/0.129	Max./min. Residual electron density [$epm^{-3}x10^{-6}$]	0.128/-0.124

Table 5.1. ^{11}B, ^{13}C and ^{29}Si NMR data [a] of 1-silacyclopent-2-ene **89 - 91**

	δ ^{13}C (C-2)	δ ^{13}C (C-3)	δ ^{13}C (C-4)	δ ^{13}C (C-5)	δ ^{11}B	δ ^{29}Si
89a [b]	144.9 [70.0]	170.5 (br)	34.0	12.7 [61.1]	85.8	38.2
89b [c]	148.3 [71.7]	170.1 (br)	33.0	13.1 [60.3]	85.1	37.0
89c [d]	146.4 [69.8]	174.6 (br)	33.1	13.3 [60.7]	85.2	37.4
90a [e]	143.5 [71.6]	172.7 (br)	32.3	12.9 [61.9]	86.0	27.3
90c [f]	144.7 [71.8]	176.7 (br)	33.3	13.5 [61.9]	86.2	25.8
91a [g]	144.9 [70.0]	170.5 (br)	33.5	12.7 [61.1]	85.8	38.2
91c [h]	146.4 [69.8]	174.6 (br)	33.1	13.3 [60.7]	85.2	37.4

[a] Measured in C_6D_6 at 23°C, (br) indicates the ^{13}C NMR signal broadened by partially relaxed ^{11}B-^{13}C spin-spin coupling; [97,98] coupling constants belonging to $^{1}J(^{13}C,^{29}Si)$ are given in square brackets; [b] Other ^{13}C data : δ [$J(^{13}C,^{29}Si)$] = 2.6 [55.2, Si-Me], 32.0 [7.1], 31.9, 23.4, 14.3 (Bu), 33.8, 33.8, 32.3 (br), 23.4 (9-BBN); [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 4.8 [54.9, Si-Me], 33.6, 32.6 (br), 23.7 (9-BBN), 35.5, 33.9 (^{t}Bu); [d] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 1.9 [56.7, Si-Me], 34.5, 34.3, 32.5 (br), 23.5 (9-BBN), 141.5, 128.6, 128.2, 126.8 (*i, o, m, p,* Ph); [e] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 33.8, 32.5 (br), 23.5 (9-BBN), 33.9, 32.1, 23.3, 14.1 (Bu), 135.2 [74.6], 134.3, 130.5, 128.4 (*i, o, p, m,* Si-Ph); [f] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 34.5, 34.6, 32.7 (br), 23.5 (9-BBN), 141.2 [6.6], 134.7 [64.5], 134.3, 130.7, 128.49, 128.46, 128.40, 126.9 (Ph, Si-Ph); [g] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 33.8, 32.3 (br), 23.3 (9-BBN), 32.0 [7.2], 31.0, 29.9, 14.1 (Bu); [h] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 34.4, 32.5 (br), 23.4 (9-BBN), 139.0, 128.7, 128.4, 127.4 (*i, o, m, p*, Ph).

Table 5.2. Crystal data and structure refinement for **89c**.

Formula	$C_{19}H_{26}BClSi$	Formula weight	328.75
Crystal	Prism	Dimensions [mm]	0.73x0.64x0.60
Crystal system	Monoclinic	Space group	P21/n
Temperature [K]	133(2)	*Z*	4
Lattice parameters		Absorption coef. [mm^{-1}]	0.280
a [pm]	926.70 (6)	Measuring range [°]	2.2-25.7
b [pm]	1639.11	Volume [$Å^3$]	1759.01 (19)
c [pm]	1178.22(7)	Density [Mg/m^3]	1.241
α [°]	90.00	Completeness to θ	25.7°:99.5 %
β [°]	100.622 (5)	Goodness-of-fit on F^2	1.067
γ [°]	90.00		
F(000)	704	Reflections collected	23567
Refined parameters	199	Reflections with $I>2\sigma(I)$	3006
Diffractometer	STOE IPDS II	Wave length [pm]	71.069
wR_2/R_1 [$I>2\sigma(I)$]	0.0390/0.1048	Max./min. Residual electron density [$epm^{-3}x10^{-6}$]	0.505/-0.337

Table 5.3. ^{11}B, ^{13}C and ^{29}Si NMR data [a] of alkyn-1-yl-substituted 1-silacyclopent-2-ene, **92** and **93**.

	92a [b]	**92c** [c]	**93a** [d]	**93c** [e]
δ ^{13}C (C-2)	148.0 [67.5]	147.7 [67.9]	146.3 [68.9]	145.9 [69.6]
δ ^{13}C (C-3)	167.7 (br)	172.9 (br)	170.1 (br)	175.3 (br)
δ ^{13}C (C-4)	34.2	34.8	34.0	35.2
δ ^{13}C (C-5)	11.1 [58.6]	11.5 [58.9]	11.5 [59.7]	12.1 [60.0]
δ ^{13}C (≡C)	109.5 [15.9]	108.1 [16.0]	111.7 [16.7]	109.8 [16.4]
δ ^{13}C (Si-C≡)	83.4 [84.7]	92.8 [83.1]	81.2 [89.6]	90.6 [88.6]
δ ^{29}Si	-6.0	-4.1	-9.1	-8.3
δ ^{11}B	85.6	86.1	85.1	84.5

[a] Measured in C_6D_6 at 23 °C, (br) indicates a broad NMR signal owing to partially relaxed ^{11}B,^{13}C scalar coupling; [97,98] some coupling constants $^{1}J(^{13}C,^{29}Si)$ and $^{2}J(^{13}C,^{29}Si)$ are given in square brackets; [b] Other ^{13}C NMR data: δ [$J(^{13}C,^{29}Si)$] = -0.4 [54.3, Si-Me], 32.8 [6.4], 33.6, 31.0, 22.2, 20.0, 14.4, 13.7 (Bu), 33.8, 32.3 (br), 23.6 (9-BBN); [c] Other ^{13}C NMR data: δ [$J(^{13}C,^{29}Si)$] = -1.0 [55.8, Si-Me], 34.6, 34.3, 32.5 (br), 23.6 (9-BBN), 142.9 [6.0, *i*], 123.6 (*i*), 132.3, 128.8, 128.5, 128.5, 128.4, 126.6 (Ph); [d] Other ^{13}C NMR data: δ [$J(^{13}C,^{29}Si)$] = 34.0, 32.9, 23.4, 14.3 (=C-Bu), 30.9, 22.3, 20.1, 13.7 (≡C-Bu), 33.8, 32.4 (br), 23.6 (9-BBN), 136.8 [71.9], 134.9, 128.2, 129.8, (*i, o, m, p,* Si-Ph); [e] Other ^{13}C NMR data: δ [$J(^{13}C,^{29}Si)$] = 34.6, 34.5, 32.6 (br), 23.6 (9-BBN), 142.5 [6.1, *i*], 135.6 [73.7, *i*], 123.2 (*i*), 135.0, 132.4, 130.2, 129.1, 128.6, 128.5, 128.4, 128.37, 126.6 (Si-Ph, Ph).

Table 5.4. ^{11}B, ^{13}C and ^{29}Si NMR data [a] of 1-(alkenyl)-1-silacyclopent-2-ene **94** and **95**.

	94a [b]	**94c** [c]	**95a** [d]	**95c** [e]
$\delta^{13}C$ (C-2)	151.1 [60.6]	151.6 [61.1]	148.6 [61.8]	149.1 [62.1]
$\delta^{13}C$ (C-3)	166.5 (br)	171.1 (br)	169.1 (br)	174.6 (br)
$\delta^{13}C$ (C-4)	32.2	33.8	32.0	34.5
$\delta^{13}C$ (C-5)	12.4 [53.9]	13.0 [53.0]	12.2 [53.4]	11.8 [53.9]
$\delta^{13}C$ ((B)C=)	148.9 [53.9, br]	152.5 (br)	146.5 (br)	149.4 (br)
$\delta^{13}C$ (=C)	157.4	152.9	159.9	155.6
$\delta^{29}Si$	7.3	9.0	3.1	4.1
$\delta^{11}B$	84.4	85.3	85.6	85.4

[a] Measured in C_6D_6, (br) indicates a broad NMR signal, [97,98] coupling constants $^1J(^{13}C,^{29}Si)$ are given in parentheses; [b] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 1.5 [49.3, Si-Me], 33.81, 33.80, 33.79, 33.78, 32.3 (br), 23.6, 23.7 (9-BBN), 35.2, 34.9, 33.7, 33.4, 24.3, 23.8, 14.4, 14.3 (Bu); [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 1.0 [51.7, Si-Me], 34.8, 34.5, 34.5, 34.4, 32.4 (br), 23.7 (9-BBN), 143.6 (*i*), 141.3 (*i*), 128.6, 128.3, 128.2, 128.16, 129.3 (*p*), 126.2 (*p*) (Ph); [d] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 34.6, 34.4, 34.0, 33.9, 32.3 (br), 31.5 (br), 23.7, 23.6 (9-BBN), 36.0, 35.0, 34.1, 33.7, 23.6, 23.0, 14.2, 14.2 (Bu), 140.5 [64.1], 134.6, 128.1, 129.0 (*i, o, m, p,* Si-Ph); [e] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 34.8, 34.7, 34.4, 34.3, 32.5 (br), 32.1 (br), 23.7, 23.7 (9-BBN), 144.1 [5.9. *i*], 140.7, 140.6, 134.8, 134.3, 129.8, 128.5, 128.5, 128.4, 128.4, 128.3, 128.1 (Si-Ph, Ph).

Table 5.5. ^{11}B, ^{13}C and ^{29}Si NMR data [a] of 1-silacyclohex-2-enes **96c** and **97c**.

	96c [b]	**97c** [c]
δ ^{13}C (C-2)	139.6 [67.1]	144.2 [60.2]
δ ^{13}C (C-3)	170.0 (br)	168.4 (br)
δ ^{13}C (C-4)	32.3	31.9
δ ^{13}C (C-5)	21.7	22.4
δ ^{13}C (C-6)	12.4 [56.3]	12.7 [51.5]
δ ^{13}C (9-BBN)	23.6, 32.8 (br), 34.4, 34.6	34.8, 34.6, 34.6, 34.2, 32.7 (br), 31.8 (br), 23.6, 23.6
δ ^{13}C (Si-Me)	-2.1 [57.9]	-0.3 [52.2]
δ ^{29}Si	-34.3	-24.3
δ ^{11}B	85.7	85.4

[a] Measured in C_6D_6 at 23 °C, (br) stands for broad and indicates the ^{13}C NMR signal broadened by partially relaxed ^{11}B-^{13}C spin-spin coupling, [97,98] $J(^{13}C,^{29}Si)$ spin-spin coupling constants are given in square brackets; [b] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 93.3 [85.4, ≡C-Si], 107.1 [16.1, C≡], 123.9, 132.3, 128.4, 128.6 (*i, o, m, p,* ≡C-Ph), 146.0, 129.0, 128.4, 126.4 (*i, o, m, p,* Ph); [c] Other ^{13}C data: δ = 152.1 (br, (B)C=), 152.9 (=C), 146.8, 141.2, 129.7, 129.3, 128.3, 128.2, 128.1, 126.1 (Ph).

Table 5.6. ^{11}B, ^{13}C and ^{29}Si NMR data [a] for intermediates **98a** and **99a**.

	δ ^{13}C (C-2)	δ ^{13}C (C-3)	δ ^{13}C (C-4)	δ ^{13}C(C-5)	δ ^{29}Si	δ ^{11}B
98a [b]	146.8 [67.5]	169.2 (br)	34.1	10.4 [60.3]	-11.8	85.6
99a [c]	146.1 [69.4]	174.6 (br)	35.0	10.9 [59.9]	-10.9	86.0

[a] Measured in C_6D_6 at 23°C, (br) indicates the ^{13}C NMR signal broadened by partially relaxed ^{11}B-^{13}C spin-spin coupling, [97,98] coupling constants corresponding to $^1J(^{13}C,^{29}Si)$ are given in square brackets; [b] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 136.3 [69.9, =CH], 134.3 ($=CH_2$), 110.7 [16.3, C≡], 80.9 [89.6, Si–C≡], 31.0, 22.3, 20.1, 13.8 (≡C-Bu), 33.7, 32.9, 23.5, 14.4 ((C-2)–Bu), 34.0, 34.0, 32.5 (br), 23.6 (9-BBN); [c] Other ^{13}C data: δ [J ($^{13}C,^{29}Si$)] = 34.5, 34.6, 32.5 (br), 23.6 (9-BBN), 109.3 [16.2, ≡C], 90.4 [87.8, Si–C≡], Other carbons are without assignment.

Table 5.7. ^{11}B, ^{13}C and ^{29}Si NMR data [a] of 1,6-diorgano-5-silaspiro[4.4]nona-1,6-diene derivatives **100** and **101**.

	$\delta^{13}C$ (C-1,6)	$\delta^{13}C$ (C-2,7)	$\delta^{13}C$ (C-3,8)	$\delta^{13}C$ (C-4,9)	$\delta^{29}Si$	$\delta^{11}B$
100a [b]	149.1 [58.2]	168.5 (br)	34.3	9.4 [50.8]	34.9	85.6
100c [c]	149.7 [58.9]	173.5 (br)	35.2	9.3 [51.8]	33.2	86.0
100e [d]	149.6 [59.3]	173.0 (br)	34.5	9.3 [52.5]	35.8	87.0
101a [e]	150.0 [58.2] 148.8 [58.9]	172.4 (br) 169.0 (br)	34.6 34.9	10.4 [49.9] 8.8 [52.3]	35.6	86.4

[a] Measured in C_6D_6 at 23°C, (br) indicates the ^{13}C NMR signal broadened by partially relaxed ^{11}B-^{13}C spin-spin coupling, [97,98] coupling constants corresponding to $^1J(^{13}C,^{29}Si)$ are given in square brackets; [b] Other ^{13}C data: δ = 33.9, 33.9, 32.4 (br), 23.7 (9-BBN), 33.8, 33.2, 23.7, 14.4 (Bu); [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 34.3, 34.8, 32.7 (br), 23.7 (9-BBN), 143.7 [6.3], 128.4, 128.2, 126.4 (*i*, *o, m, p,* Ph); [d] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 34.9, 34.4, 32.7 (br), 23.8 (9-BBN), 140.9 [6.7], 128.2, 125.3, 149.1, 35.2, 31.5 (*i, o, m, p, $C_{tert.}$, Me*, 4-^{t}Bu-C_6H_4); [e] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 34.6, 33.4, 23.9, 14.4 (Bu), 33.9, 33.8, 32.7 (br), 32.5 (br), 23.8, 23.7 (9-BBN), 141.1 [6.3], 128.2, 125.1, 148.9, 34.1, 31.7 (*i, o, m, p, $C_{tert.}$*, *Me*, 4-^{t}Bu-C_6H_4).

Table 5.8. Crystal data and structure refinement for **100c**.

Formula	$C_{36}H_{46}B_2Si$	Formula weight	528.44
Crystal	Prism	Dimensions [mm]	0.47×0.36×0.35
Crystal system	Triclinic	Space group	P-1
Temperature [K]	133 (2)	*Z*	2
Lattice parameters		Absorption coef. [mm^{-1}]	0.103
a [pm]	996.93 (9)	Measuring range [°]	1.7-25.7
b [pm]	1248.30 (9)	Volume [$Å^3$]	1493.4 (2)
c [pm]	1369.00 (10)	Density [Mg/m^3]	1.175
α [°]	113.532 (5)	Completeness to θ	25.7°:98.8 %
β [°]	104.845 (6)	Goodness-of-fit on F^2	1.044
γ [°]	91.623 (6)		
F(000)	572	Reflections collected	20118
Refined parameters	352	Reflections with $I>2\sigma(I)$	4759
Diffractometer	STOE IPDS II	Wave length [pm]	71.069
wR_2/R_1 [$I>2\sigma(I)$]	0.0400/0.1063	Max./min. Residual electron density [$epm^{-3}x10^{-6}$]	0.380/-0.302

Table 6.1. ^{11}B, ^{13}C and ^{29}Si NMR data [a] for silols **102 - 108**

	δ ^{13}C (C-2)	δ ^{13}C (C-3)	δ ^{13}C (C-4)	δ ^{13}C (C-5)	δ ^{29}Si	δ ^{11}B
102c [b]	143.9 [63.8]	170.6 (br)	158.1 [10.1]	138.1 [67.2]	-12.2	87.2
102d [c]	143.6 [63.9]	169.8 (br)	157.8 [10.5]	137.6 [67.5]	-12.7	87.1
103a [d]	138.7 [54.7]	169.8 (br)	157.4 [10.9]	134.9 [68.9]	-14.9	86.4
103c [e]	142.3 [65.1]	172.0 (br)	159.6 [10.5]	137.1 [68.4]	-12.9	86.8
104a [f]	140.9 [64.5]	168.1 (br)	155.9 [11.2]	136.5 [69.9]	-0.4	87.1
104c [g]	140.9 [58.2]	170.4 (br)	157.9 [10.1]	134.7 [65.6]	1.9	87.0
105a [h]	140.0 [65.9]	169.6 (br)	157.6 [11.3]	134.8 [67.5]	-4.6	86.5
106c [i]	141.9 [79.5]	172.1 (br)	159.7 [n. m.]	136.2 [n. m.]	-6.6	86.7
107a [j]	136.6 [72.5]	167.1 (br)	155.4 [15.1]	132.5 [78.1]	16.7	86.1
108a [k]	136.6 [73.6]	169.0 (br)	157.2 [15.0]	132.7 [79.4]	5.3	86.8
109c [l]	146.1 [64.5][m]	173.3 (br)	169.1 [9.1]	132.2 [67.7]	-13.5 (br) [m]	88.1

[a] Measured in C_6D_6, coupling constants corresponding to $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$ are given in square brackets, n. m. means not measured owing to some unknown side reactions, (br) indicates a broad ^{13}C resonance signal of carbon atom linked to boron; [97,98] [b] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = –6.8 [49.8, Si-Me], 22.3 (br), 9.7 (BEt_2), 24.7, 14.3 (Et), 141.7 [6.6, *i*], 140.6 [6.0, *i*], 128.80, 128.77, 128.02, 128.00, 126.5 (*p*), 126.0 (*p*) (Ph); [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = -6.6 [49.6, Si-Me], 22.3 (br), 9.8 (BEt_2), 24.8, 14.4 (Et), 138.9 [6.6], 137.7 [6.1], 129.6, 129.5, 128.6, 128.0, 135.9, 135.2, 21.2, 21.1 (*i, i, o, o, m, m, p, p,* Me, Me, *p*-Tolyl), [d] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 22.9 (br), 9.4 (BEt_2), 24.9, 14.1 (Et), 34.9, 34.3, 32.6, 28.8, 23.3, 23.3, 14.2, 14.2 (Bu), 134.0 [63.5], 135.6, 128.5, 129.8, (*i, o, m, p,* Si-Ph); [e] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 22.3 (br), 9.9 (BEt_2), 22.3, 14.3 (Et), 141.4 [6.7, *i*], 140.2 [5.9, *i*], 128.72, 128.65, 128.64, 128.63, 126.6 (*p*), 126.1 (*p*) (Ph), 131.9 [67.4], 135.7, 128.3, 128.7 (*i, o, m, p,* Si-Ph); [f] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = -5.5 [49.4, Si-Me], 34.0, 33.4, 32.7, 28.8, 23.3, 23.3, 14.1, 14.2 (Bu), 22.8 (br), 9.4 (BEt_2), 24.7, 14.2 (Et), 136.3 [62.9], 134.5, 128.3, 129.5, (*i, o, m, p,* Si-Ph); [g] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = -6.4 [51.4, Si-Me], 22.3 (br), 9.9 (BEt_2), 24.8, 14.5 (Et),140.1, 134.8, 128.7, 130.0, (*i, o, m, p,* Si-Ph), 145.0, 141.9, 128.7, 128.6, 128.2, 127.7, 125.9, 126.4 (*i, i, o, o, m, m, p, p,* Ph); [h] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 22.9 (br), 9.5 (BEt_2), 24.9, 14.0 (Et), 34.0, 33.4, 33.2, 29.1, 23.3, 14.2, 14.1 (Bu), 135.8 [62.1], 135.9, 128.4, 129.8, (*i, o, m, p,*

$SiPh_2$); [i] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 9.0, 22.3 (BEt_2), 13.7, 27.1 (Et), Ph carbons without assignment; [j] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 0.8 [69.5, Si-Me], 22.6 (br), 9.1 (BEt_2), 24.7, 13.6 (Et), 33.4, 32.9, 31.6, 27.8, 23.4, 14.3, 14.2 (Bu); [k] Other ^{13}C are not assigned as some side reactions including formation of 1-silacyclobutene take place; [l] Other ^{13}C data: δ = 11.3, 21.7, 22.0 (br), 22.3 (br), 30.6, 34.9, 35.0 (br) (9-Et-9-BBN), 142.8 [br, 6.9, *i*], 140.6 [br, 6.0, *i*], 135.8, 132.1 [br, 67.7, *i*], 130.4, 128.7, 128.7, 128.6, 128.3, 126.9, 126.0 (Ph, Si-Ph); (br) [m]. represent broad signals owing to exchange process.

Table 6.2. Crystal data and structure refinement for silole **109c.**

Formula	$C_{32}H_{35}BSi$	Formula weight	458.50
Crystal	Prism	Dimensions [mm]	0.35x0.16x0.15
Crystal system	Monoclinic	Space group	P2(1)/c
Temperature [K]	133(2)	*Z*	4
Lattice parameters		Absorption coef. [mm^{-1}]	0.11
a [pm]	961.60 (10)	Measuring range [°]	1.8–25.7
b [pm]	1524.8 (2)	Volume [$Å^3$]	2591.2 (5)
c [pm]	1808.3 (2)	Density [Mg/m^3]	1.175
$\alpha = \gamma$ [°]	90.00		
β [°]	102.2 (9)		
Completeness to θ	25.7°:95.1 %	Goodness-of-fit on F^2	1.16
F(000)	984	Reflections collected	14705
Refined parameters	447	Reflections with $I>2\sigma(I)$	2825
Diffractometer	STOE IPDS II	Wave length [pm]	71.069
wR_2/R_1 [$I>2\sigma(I)$]	0.089/0.157	Max./min. Residual electron density [$epm^{-3}x10^{-6}$]	0.23/-0.25

Table 6.3. ^{11}B, ^{13}C, ^{29}Si NMR data [a] of silols **111 - 112**

	δ^{13}C (C-2)	δ^{13}C (C-3)	δ^{13}C (C-4)	δ^{13}C (C-5)	δ^{29}Si	δ^{11}B
111a [b]	141.9 [63.0]	169.1 (br)	156.1 [11.2]	138.9 [70.6]	-24.4	87.1
111c [c]	139.9 [53.6]	171.8 (br)	159.7 [11.0]	136.9 [74.9]	–23.0	86.7
112a [d]	142.2 [62.9]	167.3 (br)	155.0 [10.3]	137.4 [67.2]	-0.8	86.9
112c [e]	145.4 [64.6]	169.3 (br)	157.5 [9.5]	139.7 [67.3]	-1.8	88.0

[a] Measured in C_6D_6, coupling constants $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$ are given in square brackets, (br) denotes a broad ^{13}C resonance signal as a result of partially relaxed scalar ^{11}B-^{13}C coupling; [97,98] [b] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 111.6 [26.1, ≡C], 79.0 [90.4, Si-C≡], 135.6, 135.1, 128.3, 129.8 (Si-Ph), other carbons without assignment; [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 22.3 (br), 9.9 (BEt_2), 25.0, 14.2 (Et), 110.7 [16.8, ≡C], 87.5 [91.9, Si-C≡], 141.8, 141.0, 139.4, 136.9, 135.3, 132.6, 130.6, 128.8, 128.7, 128.7, 128.7, 128.4, 128.2, 126.7, 126.3, 122.9 (Si-Ph, Ph); [d] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = -3.3 [47.2, Si-Me], 34.2, 33.9, 33.7, 33.3, 31.6, 29.3, 23.8, 22.8, 14.4, 14.3 (Bu), 22.8 (br), 21.7 (br), 9.6, 9.4 (BEt_2), 24.6, 24.1, 14.1, 13.8, (Et), 133.4 [66.6, =C-Si], 165.2 (br, BC=); [e] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = -3.8 [48.6, Si-Me], 22.3 (br), 21.6 (br), 9.8, 9.4 (BEt_2), 24.7, 24.5, 14.3, 13.4 (Et), 143.2 [4.5], 142.3 [6.4], 141.3 [5.8], (other Ph carbons are without assignment), 135.5 [67.2, Si-C=],170.0 [br, =C-B].

Table 6.4. ^{11}B, ^{13}C and ^{29}Si NMR data [a] for silols **114 - 118**

	δ^{13}C (C-2)	δ^{13}C (C-3)	δ^{13}C (C-4)	δ^{13}C (C-5)	δ^{29}Si	δ^{11}B
114a [b]	140.1 [65.0]	167.7 (br)	155.5 [11.2]	135.8 [69.5]	-3.5	86.8
114c [c]	144.6 [64.3]	169.9 (br)	157.6 [10.1]	139.2 [68.0]	-1.1	85.1
115a [d]	139.7 [65.9]	169.2 (br)	157.0 [11.1]	135.7 [62.6]	-8.4	86.5
116c [e]	144.7 [63.2]	169.7 (br)	157.5 [9.7]	139.0 [66.5]	6.9	86.5
117a [f]	140.2 [62.4]	167.4 (br)	155.0 [8.8]	135.6 [67.1]	9.7	85.6
117c [g]	145.3 [64.4]	169.7 (br)	157.3 [9.2]	139.5 [65.1]	12.3	85.1
118a [h]	140.3 [62.7]	167.4 (br)	155.1 [10.1]	135.6 [67.1]	9.6	87.9

[a] Measured in C_6D_6 at 23 °C, Some coupling constants $^1J/^2J(^{13}C,^{29}Si)$ are given in square brackets, (br) denotes a broad ^{13}C resonance signal as a result of partially relaxed scalar ^{11}B-^{13}C coupling; [97,98] [b] Other ^{13}C NMR data: δ [$J(^{13}C,^{29}Si)$] = -5.7

[49.3, Si-Me], 22.8 (br), 9.2 (BEt_2), 24.7, 14.2 (Et), 34.2, 33.6, 32.8, 28.8, 23.5, 23.49, 14.4, 14.3 (Bu), 133.1 (=CH_2), 137.2 [61.3, Si-CH=]; [c] Other ^{13}C NMR data: δ [$J(^{13}C,^{29}Si)$] = -6.5 [51.3, Si-Me], 22.3 (br), 9.8 (BEt_2), 24.7, 14.5 (Et), 142.0 [6.5], 141.0 [6.0], 128.7, 128.7, 128.3, 127.7, 126.4, 125.9 (*i, i, o, o, m, m, p, p,* Ph), 135.3 (=CH_2), 135.1 [63.7, Si-CH=]; [d] Other ^{13}C NMR data: δ [$J(^{13}C,^{29}Si)$] = 22.8 (br), 9.4 (BEt_2), 24.9, 14.1 (Et), 34.1, 33.5, 33.0, 29.0, 23.3, 14.1 (Bu), 135.2, 135.15, 128.3, 129.7, (*i, o, m, p,* Si-Ph), 135.0 (=CH_2), 133.9 [63.8, Si-CH=]; [e] Other ^{13}C NMR data: δ [$J(^{13}C,^{29}Si)$] = -5.4 [49.5, Si-Me], 22.3 (br), 9.8 (BEt_2), 24.6, 14.5 (Et), 133.8 (=CH), 114.0 (H_2C=), 21.2 [46.2, Si-CH_2], 142.3 [6.7, *i*], 141.4 [5.9, *i*], 128.8, 128.7, 128.3, 127.6, 126.4 (*p*) 125.9 (*p*) (Ph); [f] Other ^{13}C NMR data: δ [$J(^{13}C,^{29}Si)$] = -3.9 [46.3, Si-Me], 34.2, 33.2, 29.1, 23.61, 23.6, 14.4 (Bu), 22.8 (br), 9.4 (BEt_2), 23.7, 13.4 (Et), 19.5 (br), 8.5 (BEt_2), 19.5 (br, B-CH_2), 6.6 [49.1, Si-CH_2]; [g] Other ^{13}C NMR data: δ [$J(^{13}C,^{29}Si)$] = -4.8 [48.5, Si-Me], 22.4 (br), 10.0 (BEt_2), 24.7, 14.7 (Et), 19.5 (br), 8.5 (BEt_2), 6.1 [51.1, Si-CH_2], 19.4 (br, CH_2-B), 142.6 [6.4], 141.7 [5.8], 128.7, 128.8, 128.1, 127.5, 126.3, 125.8 (*i, i, o, o, m, m, p, p,* Ph); [h] Other ^{13}C NMR data: δ [$J(^{13}C,^{29}Si)$] = -4.0 [46.1, Si-Me], 22.8 (br), 8.5 (BEt_2), 24.7, 14.4 (Et), 6.5 [49.0, Si-CH_2], 20.6 (br, B-CH_2), 34.2, 33.7, 33.2, 29.2, 23.7, 23.6, 14.4, 14.4 (Bu), 33.7, 31.5 (br), 23.8 (9-BBN).

Table 6.5. ^{11}B, ^{13}C and ^{29}Si NMR data [a] for silols **119** and **120.**

	119a [b]	**119c** [c]	**119e** [d]	**120a** [e]	**120a´** [f]
$\delta^{13}C$ (C-2)	139.1 [66.3]	143.1 [65.7]	142.4 [66.4]	139.9 [66.9]	141.5 [65.7]
$\delta^{13}C$ (C-3)	168.8 (br)	170.9 (br)	170.3 (br)	170.5 (br)	168.6 (br)
$\delta^{13}C$ (C-4)	156.7 [11.0]	158.6 [10.2]	158.4 [10.3]	157.0 [10.7]	158.0 [10.5]
$\delta^{13}C$ (C-5)	135.1 [70.6]	138.1 [69.2]	137.5 [69.6]	137.6 [69.8]	135.8 [n.o.]
$\delta^{13}C$ (Si-CH)	134.5 [63.8]	132.6 [66.4]	133.1 [66.1]	134.0 [64.7]	133.6 [64.9]
$\delta^{13}C$ (=CH_2) [g]	134.4	136.7	136.5	135.5	135.6
$\delta^{11}B$	87.1	86.2	86.9	86.3	86.3
$\delta^{29}Si$	-11.7	-10.0	-10.2	-10.8	-10.5

[a] Measured in C_6D_6 at 23 °C, coupling constants $J(^{13}C,^{29}Si)$ are given in square brackets [±0.4 Hz], n.o. means not observed owing to low concentration; (br) denotes broad ^{13}C NMR signals owing to partially relaxed scalar ^{11}B-^{13}C spin-spin coupling;

[97,98] [b] Other ^{13}C NMR data: δ [$J(^{13}C,^{29}Si)$] = 22.8 (br), 9.3 (BEt_2), 24.8, 14.1 (Et), 34.3, 33.7, 32.9, 29.0, 23.5, 23.4, 14.3, 14.2 (Bu); [c] Other ^{13}C NMR data: δ [$J(^{13}C,^{29}Si)$] = 22.2 (br), 9.8 (BEt_2), 24.8, 14.4 (Et), 141.9 [6.4], 140.9 [5.8], 128.7, 128.7, 128.5, 128.0, 126.5, 125.0 (*i, i, o, o, m, m, p, p,* Ph); [d] Other ^{13}C NMR data: δ [$J(^{13}C,^{29}Si)$] = 22.2 (br), 9.9 (BEt_2), 24.9, 14.5 (Et), 138.0 [5.3], 138.9 [6.7], 128.4, 128.0, 125.6, 125.6, 149.0, 148.4, 34.5, 34.5, 31.6, 31.5 (*i, i, o, o, m, m, p, p,* $C_{tert.}$, $C_{tert.}$, Me_3, Me_3, 4-^{t}Bu-C_6H_4); [e] Other ^{13}C NMR data: δ [$J(^{13}C,^{29}Si)$] = 22.1 (br), 9.8 (BEt_2), 24.6, 14.3 (Et), 34.5, 29.2, 23.5, 14.3 (Bu), 139.0, 128.0, 125.6, 148.5, 33.6, 31.5 (*i, o, m, p,* $C_{tert.}$, Me_3, 4-^{t}Bu-C_6H_4); [f] Other ^{13}C NMR data: δ [$J(^{13}C,^{29}Si)$] = 22.8 (br), 9.4 (BEt_2), 25.3, 14.3 (Et), 34.2, 31.2, 23.4, 14.3 (Bu), 138.2, 128.4, 125.5, 148.1, 33.0, 31.6 (*i, o, m, p*, $C_{tert.}$, Me_3, 4-^{t}Bu-C_6H_4); [g] $^2J(^{13}C,^{29}Si)$ < 5 Hz.

Table 7.1. NMR data [a] of compounds **121** and **123**

	121 [a]	**123** [b]
δ^{13}C NMR data	0.1 [57.7, Si-Me], 34.9, 33.3, 32.2, 31.7, 25.1, 24.5, 22.4 (br), 21.7 (br) (9-BBN), 152.8 (br, =C(B)), 150.1 (HC=), 143.1, 138.9, 138.2, 133.6, 128.6, 128.1, 127.5, 127.2 (Si-Ph, Ph), 159.0, 143.8, 126.4, 115.5, 112.4 (2-aminopyridyl)	133.9, 134.5, 127.4, 129.7 (*i, o, m, p,* $SiPh_2$)
δ^{11}B	-0.4	17.3
δ^{29}Si	-10.3	-44.4

[a] Measured in C_6D_6, coupling constants are given in square brackets; [b] measured in $CDCl_3$.

Table 7.2. Crystal data and structure refinement of compounds **121 - 123**.

Formula	$C_{34}H_{39}BN_2Si$ (**121**)	$C_{24}H_{45}B_3O_3$ (**122**)	$C_{72}H_{52}B_2O_9Si_6$ (**123**)
Formula weight	514.57	414.03	1251.30
Crystal	Prism	Needle-like	Prism
Dimensions [mm]	0.26x0.19x0.18	0.63x0.19x0.08	0.36x0.36x0.31
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	C(2)/c
Temperature [K]	293 (2)	191 (2)	191 (2)
Z	2	2	4
Lattice parameters			
a [pm]	693.13 (14)	661.50 (10)	2334.30 (10)
b [pm]	1081.6 (2)	1082.90 (17)	1381.00 (9)
c [pm]	2046.8 (4)	1772.2 (3)	2034.40 (14)
α [°]	80.39 (3)	76.610 (12)	90.00
β [°]	89.92 (3)	84.688 (12)	98.251
γ [°]	80.20 (3)	87.811 (13)	90.00
Absorption coef. [mm^{-1}]	0.10	0.069	0.187
Measuring range [°]	1.9-26.1	1.9-25.7	1.7-25.8
Volume [$Å^3$]	1490.2 (5)	1229.5 (3)	6490.3 (7)
Density [Mg/m^3]	1.147	1.118	1.281
F(000)	552	456	2600
Goodness-of-fit on F^2	0.832	0.766	1.034
Completeness to θ	26.1°:91.8 %	25.7°:98.9 %	25.8°:98.6 %
Reflections collected	10526	15648	41495
Reflections with $I>2\sigma(I)$	2996	1619	4083
Refined parameters	343	451	394
Diffractometer	STOE IPDS I	STOE IPDS II	STOE IPDS II
Wave length [pm]	71.073	71.069	71.069
wR_2/R_1 [$I>2\sigma(I)$]	0.054/0.150	0.0674/0.1074	0.0776/0.2165
Max./min. residual electron density [$epm^{-3}x10^{-6}$]	0.36/-0.18	0.140/-0.136	0.514/-0.289

Table 7.3. ^{11}B, ^{13}C, ^{29}Si and ^{119}Sn NMR data [a] of borolenes **124 - 130**.

	δ ^{13}C (C-2)	δ ^{13}C (C-3)	δ ^{13}C (C-4)	δ ^{13}C (C-5)	δ ^{11}B
124c [b]	172.0 (br)	179.6 {393.7}, {13.6}	68.4 {70.2}, {9.8}	51.9 (br) {50.4}, {30.1}	75.4
125a [c]	170.0 (br).	180.2 {403.0}, {12.2}	61.9 {69.5}, {12.4}	53.5 (br).	72.2
125c [d]	171.3 (br)	179.4 {398.9}, {14.0}	68.9 {71.4}, {10.2}	55.1 (br)	71.4
126a [e]	169.9 (br).	180.5 [402.5], [12.3]	62.2 {69.6}, {13.0}	53.8 (br)	72.3
126c [f]	170.3 (br)	180.2 {401.7}, {13.1}	68.8 {70.7}, {11.7}	56.2 (br) {35.8}	73.8
127c [g]	165.9 (br).	185.0 {401.0}, {12.3}	66.9 {66.5}, {14.2}	14.0 (br)	69.3
128a [h]	170.1 (br).	180.8 {397.8}, {10.9}	61.9 {69.6}, {10.7}	55.0 (br) {46.9}, {36.3}	72.5
128c [i]	170.8 (br).	180.5 {394.3}, {12.2}	68.9 {71.0}, {8.6}	56.2 (br) {44.0}, {31.5}	70.2
129a [j]	153.6 (br).	169.9 {9.6}	58.1 {15.4}	48.5 (br)	75.3
130c [k]	156.9 (br).	168.9 {12.2}	64.3 {12.7}	48.7 (br)	78.2

[a] Measured in C_6D_6 at 23 °C, (br) indicates a broad NMR signal owing to partially relaxed ^{11}B-^{13}C scalar coupling, [97,98] some spin-spin coupling constants corresponding to J(^{29}Si,^{119}Sn) J(^{13}C,^{119}Sn), J(^{13}C,^{29}Si) and J($^{119/117}$Sn,$^{119/117}$Sn) are given; [b] Other ^{13}C data: δ {J(^{13}C,^{119}Sn)} = -5.7 {343.5 Hz, $SnMe_3$}, -8.5 {338.2, $SnMe_3$}, 40.0 {30.8}, 33.9, 32.8, 29.2, 27.9, 25.3 (br), 25.1, 23.5 (9-BBN), 140.0 {11.9, 3.4}, 131.9, 128.7, 128.6, 128.6, 127.8 (Ph); ^{119}Sn NMR data: δ [[^4J($^{119/117}$Sn, $^{119/117}$Sn)]] = 24.6 [[37.6]], -60.9 [[36.5]]; ^{29}Si NMR data: δ [(J(^{29}Si,^{119}Sn))] = -0.4 [(32.8, 5.5)]; [c] Other ^{13}C data: δ{J(^{13}C,^{119}Sn)} = 40.6 {33.8, C-2´}, other carbons are not assigned owing to low concentration ca. 5 %; ^{119}Sn NMR data: δ [[^4J($^{119/117}$Sn,$^{119/117}$Sn)]] = 31.2 [[49.9]], -65.8 [[47.6]]; ^{29}Si NMR data: δ [(J(^{29}Si,^{119}Sn))] = 24.2 [(37.2, 8.9)]; [d] Other ^{13}C data: δ{J(^{13}C,^{119}Sn)}, [J(^{13}C,^{29}Si)] = -8.5 {337.9 Hz, $SnMe_3$}, -4.6 {341.7 Hz, $SnMe_3$}, 10.3 [68.7, Si-Me], 40.0 {31.9}, 33.8, 33.0, 29.2, 28.3, 25.5 (br), 24.9, 23.7 (9-BBN), 140.7 {13.6, 4.3, *i*}, 132.5, 129.4,

128.5, 128.4, 127.8 (Ph); ^{119}Sn NMR data: δ [[^{4}J($^{119/117}$Sn,$^{119/117}$Sn)]] = 23.6 [[40.7]], -61.1 [[36.8 Hz]], ^{29}Si NMR data: δ [(J(^{29}Si,^{119}Sn))] = 23.3 [(35.6, 7.8)]; [e] Other ^{13}C data: δ {J(^{13}C,^{119}Sn)} = -7.7 {337.4, $SnMe_3$}, -3.3 {333.9, $SnMe_3$}, 40.7 {34.6}, 34.3, 32.8, 28.9, 25.5 (br), 23.8, 23.4 (9-BBN), 36.3 {16.2}, 32.3, 25.0, 14.3 (Bu), 137.2 {10.8}, 133.6, 128.1, 130.9 (*i, o, m, p,* Si-Ph); ^{119}Sn NMR data: δ [[^{4}J($^{119/117}$Sn, $^{119/117}$Sn)]] = 33.7 [[48.7]], -66.1 [[45.5]]; ^{29}Si NMR data: δ [(J(^{29}Si, ^{119}Sn))] = 12.4 [(40.6, 8.6)]; [f] Other ^{13}C data: δ {J(^{13}C,^{119}Sn)}, [J(^{13}C,^{29}Si)] = -8.6 {337.8, $SnMe_3$}, -3.5 {340.1, $SnMe_3$}, 40.2 {31.4}, 33.6, 32.8, 29.2, 28.6, 25.5 (br), 24.9, 23.6 (9-BBN), 136.4 [93.4] {9.4}, 134.1 {5.7}, 127.4, 128.2 (*i, o, m, p,* Si-Ph), 139.8 {14.8, 4.5, *i*}, 133.5, 130.3, 129.8, 129.0, 128.2 (Ph); ^{119}Sn NMR data: δ [[^{4}J($^{119/117}$Sn,$^{119/117}$Sn)]] = 29.8 [[41.8]], -61.0 [[41.3]]; ^{29}Si NMR data: δ [(J(^{29}Si,^{119}Sn))] = 12.4 [(41.9, 7.2)]; [g] Other ^{13}C data: δ {J(^{13}C,^{119}Sn)} = -8.3 {337.3, $SnMe_3$}, -3.9 {340.1, $SnMe_3$}, 26.8 {33.8}, 16.8 {6.9} (Et), 30.2 (br), 9.0 (BEt), 138.9 {19.4, 4.5, *i*}, 133.4, 132.2, 129.3, 128.0, 127.8 (Si-Ph), 136.1 {12.4}, 133.7, 130.2, 128.7 (Ph); ^{119}Sn NMR data: δ [[^{4}J($^{119/117}$Sn,$^{119/117}$Sn)]] = 23.1 [[46.3]], -59.7 [[40.3]]; ^{29}Si NMR data: δ [(J(^{29}Si,^{119}Sn))] = 12.6 [(44.3, 8.6)]; [h] Other ^{13}C data: δ {J(^{13}C,^{119}Sn)} = -7.5 {338.0, $SnMe_3$}, -4.1 {345.8, $SnMe_3$}, 40.6 {33.9}, 35.0, 31.9, 28.7, 28.4, 25.6 (br), 23.6, 23.2 (9-BBN), 35.8 {15.5}, 30.5, 25.4, 14.3 (Bu); ^{119}Sn NMR data: δ [[^{4}J($^{119/117}$Sn,$^{119/117}$Sn)]] = 37.4 [[42.0]], -64.5; ^{29}Si NMR data: δ [(J(^{29}Si,^{119}Sn))] = 2.7 [(35.9, 10.7)]. [i] Other ^{13}C data: δ {J(^{13}C,^{119}Sn)} = 0.7 {343.7, $SnMe_3$}, 0.8 {374.6, $SnMe_3$}, 40.0 {30.8}, 33.3, 29.0, 28.2, 25.6 (br), 24.5, 24.0 (9-BBN), 139.1 {12.6, 4.2, *i*}, 133.3, 129.7, 128.2, 128.1, 127.9 (Si-Ph); ^{119}Sn NMR data: δ [[J($^{119/117}$Sn,$^{119/117}$Sn)]] = 31.6 [[37.4]], -59.9 [[35.3]]; ^{29}Si NMR data: δ [(J(^{29}Si,^{119}Sn))] = 0.2 [(37.5, 7.1)]; [j] ^{119}Sn NMR data: δ [[J($^{119/117}$Sn,$^{119/117}$Sn)]] = -1.2 [[31.2]]; ^{29}Si NMR data: δ [(J(^{29}Si,^{119}Sn))] = 23.6 [(31.2)]; [k] ^{119}Sn NMR data: δ [[J($^{119/117}$Sn,$^{119/117}$Sn)]] = –8.7 [[33.5]]; ^{29}Si NMR data: δ [(J(^{29}Si,^{119}Sn))] = 10.5 [(32.2)].

Table 7.4. ^{11}B, ^{13}C ^{29}Si and ^{119}Sn NMR data [a] of allenes **131 - 134**.

	131a [b]	**132a** [c]	**133a** [d]	**134c** [e]
δ ^{13}C (C)	74.4 {227.9}, {226.8}	74.2 {235.2}, {224.5}	93.5	93.5 {462.7}, {19.5}
δ ^{13}C (B)	200.1 {24.2}	200.4 {23.8}	202.4 {36.9}	202.2 {38.7}, {8.7}
δ ^{13}C (A)	70.5 {48.5} [94.2]	70.4 {48.6} [96.6]	104.1 {57.1}, {35.4}	109.9 {52.6}, {35.8}
δ ^{13}C (A´)	35.2 (br)	35.5 (br)	n. a.	n. a.
δ ^{11}B	84.0	82.9	82.9	84.8
δ ^{29}Si	21.7 [(34.1)]	10.0 [(34.5)]	13.5	6.3

[a] Measured in C_6D_6 at 23 °C, (br) indicates a broad NMR signal owing to partially relaxed ^{11}B-^{13}C scalar coupling, [97,98] [b] Other ^{13}C data: δ {J(^{13}C,^{119}Sn)}, [J(^{13}C,^{29}Si)] = -7.1 {349.4, $SnMe_3$}, -7.1 {347.3, $SnMe_3$}, 5.9 [73.9, Si-Me], 14.5, 19.5, 22.1, 30.0 (Bu), 34.3, 34.1, 30.9 (br), 23.8 (9-BBN); ^{119}Sn NMR data: δ [[J($^{119/117}Sn$,$^{119/117}Sn$)]] = 6.4 [[161.1, 152.3]], -0.3 [[161.7, 151.5]]; [c] Other ^{13}C data: δ {J(^{13}C,^{119}Sn)}, [J(^{13}C,^{29}Si)] = -7.2 {349.1 $SnMe_3$}, -7.3 {347.8, $SnMe_3$}, 32.8, 31.6, 23.3, 14.5 (Bu), 34.3, 34.1, 30.9 (br), 23.8 (9-BBN), 134.8, 134.6, 131.2, 128.1 (*i, o, p, m,* Si-Ph); ^{119}Sn NMR data: δ [[J($^{119/117}Sn$,$^{119/117}Sn$)]] = 7.1 [[157.1, 148.9]], 0.8 [[157.1, 148.9]]; [d] ^{119}Sn NMR data: δ = 22.8, other carbons were not assigned; [e] ^{119}Sn NMR data: δ = 6.1.

Table 7.5. NMR data [a] (^{13}C, ^{29}Si and ^{119}Sn) of butadienes **135a** and **136c**

	135a	**136c**
δ ^{13}C (C-1)	148.4 {11.3}	147.0 {11.6}
δ ^{13}C (C-2)	162.2 (br)	161.7 (br)
δ ^{13}C (C-3)	141.0 {77.5}, [84.2]	144.2 [76.6]
δ ^{13}C (C-4)	159.5 {478.0}	165.0 {473.2}
δ ^{119}Sn	-44.3	-41.7
δ ^{29}Si	12.5 [6.6]	6.3

[a] Measured in C_6D_6 at 23 °C, coupling constants are given in square brackets; br. means a broad ^{13}C resonance owing to partially relaxed ^{11}B-^{13}C scalar coupling. [97,98]

Table 7.6. Selected bond lengths (pm) and bond angles (deg.) of **124c**.and **126c**.

$C_{24}H_{39}BCl_2SiSn_2$ (**124c**)		$C_{30}H_{43}BCl_2SiSn_2$ (**126c**)	
C18-C19	156.6(7)	C2-C8	157.4(10)
C7-C19	153.1(8)	C8-C9	151.8(10)
C7-C17	135.2(8)	C9-C10	136.0(11)
C17-B1	155.3(9)	C10-B1	156.0(11)
C18-B1	155.5(9)	C2-B1	155.8(11)
C18-Sn2	223.4(6)	C2-Sn1	224.2(7)
C7-Sn1	214.3(5)	C9-Sn2	214.8(7)
C18-Si1	183.3(6)	C2-Si1	183.4(8)
Si-H	127.2	C25-Si1	185.7(8)
Si1-Cl1	206.5(2)	Si1-Cl1	206.7(3)
B1-C18-C19	105.1(5)	B1-C2-C8	103.8(6)
C7-C19-C18	105.6(5)	C9-C8-C2	105.5(6)
C17-C7-C19	112.5(5)	C10-C9-C8	112.3(7)
C7-C17-B1	110.3(5)	C9-C10-B1	109.6(7)
Si1-C18-Sn2	108.3(3)	Si1-C2-Sn1	107.2(3)
C17-B1-C13	121.3(5)	C10-B1-C15	119.8(7)
C17-B1-C18	106.2(5)	C10-B1-C2	106.2(7)
C13-B1-C18	132.5(5)	C15-B1-C2	134.0(7)
C19-C7-Sn1	121.7(4)	C8-C9-Sn2	120.6(5)

Table 7.7. Crystal data and structure refinement details for compound **124c** and **126c**.

Formula	$C_{24}H_{39}BCl_2SiSn_2$ (**124c**)	$C_{30}H_{43}BCl_2SiSn_2$ (**126c**)
Formula weight	674.73	750.82
Crystal	Prism	Prism
Dimensions [mm]	0.33x0.30x0.25	0.48x0.40x0.31
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/n	P-1
Temperature [K]	133 (2)	143(2)
Z	4	2
Lattice parameters		
a [pm]	1021.35(9)	971.70(10)
b [pm]	2441.84(17)	1042.10(10)
c [pm]	1133.14 (9)	1640.3(2)
α [°]	90.00	83.383(10)
β [°]	95.883(6)	81.228(10)
γ [°]	90.00	76.202(10)
Absorption coef. [mm^{-1}]	2.020	1.796
Measuring range [°]	1.7-25.7	2.0-25.6
Volume [$Å^3$]	2811.1 (4)	1588.8 (3)
Density [Mg/m^3]	1.594	1.569
F(000)	1344	752
Goodness-of-fit on F^2	1.105	1.367
Completeness to θ	25.7°:98.9%	25.6°:99.4%
Reflections collected	10464	20547
Reflections with $I>2\sigma(I)$	4295	5439
Refined parameters	275	325
Diffractometer	STOE IPDS II	STOE IPDS II
Wave length [pm]	71.069	71.069
wR_2/R_1 [$I>2\sigma(I)$]	0.0476/0.126	0.0607/0.1446
Max./min. residual electron density [$epm^{-3}x10^{-6}$]	2.027/-0.738	1.396/-1.257

Table 7.8. ^{13}C and ^{29}Si NMR data [a] of **88d - P**, **141** and **142**.

	88d - P	**141**	**142**
δ ^{13}C	142.9 [50.8, C-1,5], 153.2 [16.7, C-2,6], 157.5 [51.8, C-3,7], 132.2, 132.4 (=CH), 138.4, 137.2, 136.6, 134.2, 129.8, 129.7, 129.1, 129.0, 127.6, 127.0, 21.3, 21.1 (4-Me-C_6H_4).	174.9 (COO), 23.2 (CH_3), 32.6, 25.4, 23.4 (br) (9-BBN).	183.9 (br[b], COO), 21.6 (br[b], Me), 26.0 (br), 28.2, 28.0, 27.8, 27.4 (B-Oct),
δ ^{11}B	--	16.6	8.5
δ ^{29}Si	-5.6	--	--

[a] Measured in C_6D_6 at 23 °C; Coupling constants [$^1J(^{13}C,^{29}Si)$] and [$^2J(^{13}C,^{29}Si)$] are given in square brackets; [b] ^{13}C NMR signals are broadened by dynamic exchange processes.

Table 7.9. ^{13}C and ^{29}Si NMR data [a] of protodeborylated 1-silacyclopent-2-ene **89 – P** to **91 - P**

	δ ^{13}C (C-2)	δ ^{13}C (C-3)	δ ^{13}C (C-4)	δ ^{13}C (C-5)	δ ^{29}Si
89a - P [b]	142.7 [70.6]	149.0 [15.5]	32.1	12.2 [59.3]	36.6
89c - P [c]	141.6 [70.9]	149.8 [14.7]	29.5	12.2 [60.1]	36.4
90a - P [d]	141.9 [71.9]	150.6 [15.7]	31.8	12.3 [60.7]	26.0
90c - P [e]	140.2 [73.1]	151.4 [15.2]	29.8	12.6 [60.9]	25.6
91a - P [f]	141.0 [85.0]	150.6 [22.4]	31.5	13.9 [69.6]	29.6

[a] Measured in C_6D_6 at 23°C, coupling constants corresponding to $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$ are given in square brackets; [b] Other ^{13}C data: δ[$J(^{13}C,^{29}Si)$] = 2.2 [56.4, Si-Me], 31.5 [6.1], 29.1, 22.9, 14.1 (Bu); [c] Other ^{13}C data: δ[$J(^{13}C,^{29}Si)$] = 2.2 [56.8, Si-Me], 138.5 [5.5], 129.0, 127.3, 126.8 (*i*, *o*, *p*, *m*, Ph); [d] Other ^{13}C data: δ[$J(^{13}C,^{29}Si)$] = 31.5 [5.9], 29.4, 22.8, 14.1 (Bu), 134.6 [75.1], 134.1, 130.7, 128.4 (*i*, *o*, *p*, *m*, Si-Ph); [e] Other ^{13}C data: δ[$J(^{13}C,^{29}Si)$] = 137.9 [5.6, *i*], 134.3 [77.7, *i*], 134.2, 130.9, 128.9, 128.5, 127.4, 127.1 (Si-Ph, Ph); [f] Other ^{13}C data: δ[$J(^{13}C,^{29}Si)$] = 30.4 [5.8], 27.6, 22.8, 14.1 (Bu).

Table 7.10. Crystal data and structure refinement for **90c - P** and **142**

Formula	$C_{16}H_{15}ClSi$ (**90c - P**)	$C_{20}H_{36}B_2O_5$ (**142**)
Formula weight	270.82	378.12
Crystal	Prism	Prism
Dimensions [mm]	1.10x1.01x0.79	0.96x0.81x0.58
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/c	P1
Temperature [K]	133(2)	133(2)
Z	4	2
Lattice parameters		
a [pm]	1299.20(13)	883.25(8)
b [pm]	630.07(6)	1126.03(10)
c [pm]	1807.50(18)	1136.27(10)
α [°]	90.00	112.147(7)
β [°]	110.529(8)	97.648(7)
γ [°]	90.00	95.100(7)
Absorption coef. [mm^{-1}]	0.341	0.084
Measuring range [°]	1.7 - 25.6	2.0 - 25.6
Volume [$Å^3$]	1385.6 (2)	1025.43 (16)
Density [Mg/m^3]	1.298	1.166
F(000)	568	390
Goodness-of-fit on F^2	1.139	0.953
Completeness to θ	25.6°:99.8 %	25.7°:99.4 %
Reflections collected	17848	13734
Reflections with $I>2\sigma(I)$	2440	3346
Refined parameters	223	244
Diffractometer	STOE IPDS II	STOE IPDS II
Wave length [pm]	71.069	71.069
wR_2/R_1 [$I>2\sigma(I)$]	0.0335/0.0894	0.0723/0.212
Max./min. residual electron density [$epm^{-3}x10^{-6}$]	0.379/-0.346	1.299/-1.218

Table 7.11. ^{13}C and ^{29}Si NMR data [a] of 1-silacyclopent-2-ene derivatives, **92 - P** and **93 - P**

	92a - P [b]	**92c - P** [c]	**93a - P** [d]	**93c - P** [e]
$\delta^{13}C$ (C-2)	143.3 [68.1]	141.6 [69.1]	142.5 [69.4]	140.4 [70.5]
$\delta^{13}C$ (C-3)	146.7 [13.3]	148.3 [12.7]	148.6 [13.4]	150.0 [12.9]
$\delta^{13}C$ (C-4)	32.7 [5.9]	31.0	32.6	31.3
$\delta^{13}C$ (C-5)	10.4 [58.1]	10.1 [59.1]	10.8 [58.4]	10.8 [59.7]
$\delta^{13}C$ (SiC≡)	83.0 [86.4]	92.6 [84.4]	80.8 [90.9]	90.3 [89.6]
$\delta^{13}C$ (≡C)	109.3 [16.3]	108.1 [16.1]	111.7 [16.2]	109.9 [16.7]
$\delta^{29}Si$	-8.6	-6.9	-11.5	-10.5

[a] Measured in C_6D_6 at 23 °C, some coupling constants $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$ are given in square brackets; [b] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = -0.7 [55.3, Si-Me], 32.4 [7.2], 30.3, 23.0, 14.3 ((C-2)Bu), 31.0, 22.2, 20.0, 13.7 (≡C-Bu); [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = -0.9 [56.4, Si-Me], 123.4, 132.3, 129.9, 128.5 (*i, o, m, p,* ≡C-Ph), 139.7 [5.6],128.9, 127.2, 127.0 (*i, o, m, p,* (C-2)Ph); [d] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 32.1 [8.7], 30.9, 30.7, 22.9, 22.2, 20.0, 14.2, 13.7 (Bu), 136.3 [73.1], 134.9, 128.2, 129.8 (*i, o, m, p,* Si-Ph); [e] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 139.2 [5.7, *i*], 135.2 [74.5, *i*], 123.1 (*i*), 134.9, 132.4, 130.0, 129.1, 128.8, 128.5, 128.5, 127.4, 127.1 (Si-Ph, ≡C-Ph, (C-2)Ph).

Table 7.12. ^{13}C and ^{29}Si NMR data [a] of 1-silacyclopent-2-ene, **94 - P** and **95 - P**

	94a - P [b]	**94c - P** [c]	**95a - P** [d]	**95c - P** [e]
$\delta^{13}C$ (C-2)	144.7 [62.4]	144.3 [63.1]	143.7 [63.8]	142.9 [64.8]
$\delta^{13}C$ (C-3)	145.6 [11.3]	147.0 [11.2]	147.1 [11.7]	148.5 [11.3]
$\delta^{13}C$ (C-4)	32.2	31.2	30.9	31.4
$\delta^{13}C$ (C-5)	10.8 [53.7]	10.1 [54.2]	11.1 [53.1]	10.2 [56.8]
$\delta^{13}C$ (Si-C=)	127.1 [64.8]	130.1 [63.6]	124.1 [67.5]	126.1 [66.4]
$\delta^{13}C$ (=C)	150.8	148.5	152.5	149.8
$\delta^{29}Si$	2.7	5.1	-1.6	1.4

[a] Measured in C_6D_6 at 23 °C; some coupling constants $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$ are given in square brackets; [b] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = -0.6 [50.3, Si-Me], 33.8, 32.9, 32.5, 30.6, 23.1, 22.8, 14.2 (Bu); [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = -0.6 [54.0, Si-Me], 140.4, 140.1, 128.8, 128.4, 128.2, 127.9, 127.0, 126.7 (Ph); [d] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 34.5, 32.8, 32.2, 32.0, 23.0, 22.8, 21.7, 14.2, 14.2 (Bu), 138.2 [65.5], 134.7, 128.2, 129.4 (*i, o, m, p*, Si-Ph); [e] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 140.0 [5.4, *i*], 139.5 (*i*), 137.8 [67.0, *i*], 134.9, 129.8, 128.8, 128.54, 128.52, 128.3, 128.1, 127.2, 126.8, (Si-Ph, Ph).

Table 7.13. ^{13}C and ^{29}Si NMR data of 1-silacyclohex-2-ene derivatives **96c - P** and **97c - P**.

	$\delta^{29}Si$	$\delta^{13}C$(C-2)	$\delta^{13}C$(C-3)	$\delta^{13}C$(C-4)	$\delta^{13}C$(C-5)	$\delta^{13}C$(C-6)
96c - P [b]	-32.5	136.9 [67.2]	146.3 [14.1]	30.0 [5.1]	20.9	12.5 [57.7]
97c - P [c]	-22.8	140.3 [61.7]	145.4 [10.8]	31.0	21.5	12.2 [53.3]

[b] Other ^{13}C data: δ [$J(^{13}C, ^{29}Si)$] = -2.1 [57.8, Si-Me], 93.3 [85.9, ≡C-Si], 107.3 [16.2, C≡], 123.6, 132.2, 128.5, 128.8 (*i, o, m, p,* ≡C-Ph), 144.2, 128.7, 127.1, 126.5 (*i, o, m, p,* =C-Ph); [c] Other ^{13}C data: δ [$J(^{13}C, ^{29}Si)$] = -1.1 [53.2, Si-Me], 130.5 [65.2, Si-CH=], 148.3 (=CH), 144.9, 140.2, 128.7, 128.6, 128.2, 127.8, 127.1, 126.3 (Ph).

Table 7.14. ^{13}C and ^{29}Si NMR data [a] of spirosilane **100 - P**, **101 - P**.

	$\delta^{13}C$ (C-1,6)	$\delta^{13}C$ (C-2,7)	$\delta^{13}C$ (C-3,8)	$\delta^{13}C$ (C-4,9)	$\delta^{29}Si$
100a - P [b]	143.3 [59.8]	147.7 [11.5]	31.9 [5.9]	8.5 [51.1]	28.5
100c - P [c]	141.0 [60.8]	148.0 [11.2]	29.8 [5.4]	6.6 [51.7]	29.9
100e - P [d]	142.3 [61.8]	148.3 [11.2]	31.2[5.6]	8.0 [52.1]	29.8
101a - P [e]	143.8 [60.6], 141.7 [60.3]	148.2 [11.9], 147.7 [10.8]	31.0, 30.6	8.4 [50.2], 8.2 [51.8]	29.2

[a] Measured in C_6D_6 at 23°C, coupling constants corresponding to $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$ are given in square brackets; [b] Other ^{13}C data: δ = 30.4, 25.3, 23.0, 14.2 (Bu); [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 138.9 [5.5], 127.5, 125.52, 125.48 (*i, o, m, p,* Ph); [d] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 137.5 [5.3], 126.7, 125.9, 149.5, 34.4, 31.4 (*i, o, m, p, C_{tert}, Me_3*, 4-^{t}Bu-C_6H_4); [e] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 32.2, 31.1, 23.0, 14.1 (Bu), 137.6 [5.2], 126.6, 125.7, 149.3, 32.9, 31.5 (*i, o, m, p, C_{tert}, Me_3*, 4-^{t}Bu-C_6H_4).

Table 7.15. Crystal data and structure refinement for **100c - P**.

Formula	$C_{20}H_{20}Si$	Formula weight	288.45
Crystal	Prism	Dimensions [mm]	1.08×0.77×0.61
Crystal system	Monoclinic	Space group	C2/c
Temperature [K]	133(2) K	*Z*	4
Lattice parameters		Absorption coef. [mm^{-1}]	0.148
a [pm]	2094.6(2)	Measuring range [°]	2.4 - 24.6
b [pm]	572.30(10)	Volume [$Å^3$]	1496.4(4)
c [pm]	1552.5(2)	Density [Mg/m^3]	1.280
α [°]	90.00	Completeness to θ	24.6°:99.7 %
β [°]	126.478(10)	Goodness-of-fit on F^2	1.131
γ [°]	90.00		
F(000)	616	Reflections collected	8274
Refined parameters	136	Reflections with $I>2\sigma(I)$	1180
Diffractometer	STOE IPDS II	Wave length [pm]	71.069
wR_2/R_1 [$I>2\sigma(I)$]	0.0353/0.095	Max./min. Residual electron density [$epm^{-3}x10^{-6}$]	0.216/-0.387

Table 7.16. ^{13}C and ^{29}Si NMR data[a] for silols **102 – P** to **104 - P**

	$\delta^{13}C$ (OAc)	$\delta^{13}C$ (C-2)	$\delta^{13}C$ (C-3)	$\delta^{13}C$ (C-4)	$\delta^{13}C$ (C-5)	$\delta^{29}Si$
102a - P [b]	171.3, 22.0	140.3 [79.2]	144.2 [11.9]	153.9 [11.3]	130.0 [79.8]	10.6
102c - P [c]	170.1, 22.0	139.2 [74.4]	142.8 [10.9]	155.6 [10.4]	132.8 [79.0]	8.6
102d - P [d]	170.0, 22.1	138.8 [74.4]	142.0 [10.3]	155.3 [10.5]	132.2 [79.3]	8.8
103a - P [e]	170.5, 22.1	140.3 [75.4]	145.3 [11.8]	155.4 [11.6]	132.5 [76.6]	-2.9
103c-P [f]	169.6, 21.9	138.6 [76.2]	144.1 [10.8]	156.6 [10.6]	132.5 [80.5]	-5.9
104a - P [g]	--	145.2 [63.6]	144.2 [8.3]	153.9 [8.7]	134.9 [67.8]	-1.6
104c - P [h]	--	143.8 [64.2]	143.3 [7.2]	155.3 [7.9]	138.1 [67.4]	1.0

[a] Measured in C_6D_6 at 296 K, coupling constants corresponding to $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$ are given in square brackets; [b] Other ^{13}C data: $\delta[J(^{13}C,^{29}Si)]$ = -3.7 [56.9, Si-Me], 23.7, 12.9 (Et), 32.9, 32.5, 31.9, 28.2, 23.2, 23.0, 14.3, 14.2 (Bu); [c] Other ^{13}C data: $\delta[J(^{13}C,^{29}Si)]$ = -3.6 [59.8, Si-Me], 24.8, 13.1 (Et), 139.5 [5.9, *i*], 137.9 [5.9, *i*], 129.1, 128.7, 128.5, 127.1, 127.7 (*p*), 126.4 (*p*) (Ph); [d] Other ^{13}C data: $\delta[J(^{13}C,^{29}Si)]$ = -3.4 [59.6, Si-Me], 13.2, 24.9 (Et), 21.2, 21.3, 136.5 [5.9], 135.2 [5.9], 129.8, 129.5, 128.5, 127.2, 137.2, 135.2 (Me, Me, *i, i, o, o, m, m, p, p,* 4-Me-C_6H_4); [e] Other ^{13}C data: $\delta[J(^{13}C,^{29}Si)]$ = 24.1, 13.0 (Et), 32.8, 32.4, 31.7, 28.3, 23.1, 22.9, 14.2, 14.1 (Bu), 135.1, 134.3, 128.4, 130.5 (*i, o, m, p,* Si-Ph); [f] Other ^{13}C data: $\delta[J(^{13}C,^{29}Si)]$ = 25.0, 13.2 (Et), 139.3 [5.9, *i*], 137.7 [5.6, *i*], 134.8, 131.1, 129.0, 128.7, 128.6, 128.6, 127.7, 127.2, 126.4 (Si-Ph, Ph); [g] Other ^{13}C data: $\delta[J(^{13}C,^{29}Si)]$ = -6.2 [49.7, Si-Me], 13.7, 23.8 (Et), 33.3, 32.8, 32.3, 28.7, 23.2, 22.9, 14.1, 14.1 (Bu), 135.5 [64.1], 134.5, 128.3, 129.6 (*i, o, m, p,* Si-Ph); [h] Other ^{13}C data: $\delta[J(^{13}C,^{29}Si)]$ = -6.2 [51.9, Si-Me], 13.8, 24.8 (Et), 140.4 [5.8, *i*], 138.9 [5.9, *i*], 134.2 [66.5, *i*], 134.8, 130.1, 129.0, 128.7, 128.6, 128.3, 127.3, 126.9, 126.1 (Si-Ph, Ph).

Table 7.17. ^{11}B, ^{13}C and ^{29}Si NMR data [a] of oxasilaboratole **112a - P**.

	$\delta^{13}C$	$\delta^{29}Si$	$\delta^{11}B$
112a - P	176.2 (br), 149.7 (=CH), 141.0, 137.2 [70.7], 129.2 [84.9], 128.5 (=CH), 49.1 (OMe), 35.5, 33.8, 33.1, 31.7, 28.3, 28.0, 23.9, 23.3, 23.2 (br), 22.7, 22.6, 14.1, 14.0, 13.9, 13.8, 12.9, 10.5, 10.4 (Bu, BEt_2, Et), 0.5 (SiMe).	19.1	18.3
112a´ - P	176.4 (br), 145.1 (=CH), 139.3 [70.3], 139.0, 128.8, 125.7 (=CH), 48.9 (OMe), 33.4, 32.1, 31.7, 30.6, 30.3, 29.1, 28.4, 23.5, 23.3, 22.5, 21.9, 14.0, 13.9, 13.5 (br), 13.3, 13.1, 10.4, 10.2 (Bu, BEt_2, Et), 1.0 (Si-Me)	20.0	18.3

[a] Measured in $CDCl_3$ at 23 °C.

Table 7.18. ^{13}C and ^{29}Si NMR data[a] for silols **114c - P** and **116 - P**

	$\delta^{13}C$ (C-2)	$\delta^{13}C$ (C-3)	$\delta^{13}C$ (C-4)	$\delta^{13}C$ (C-5)	$\delta^{29}Si$
114c - P [b]	143.3 [63.1]	142.9 [8.3]	155.1 [7.8]	137.3 [67.5]	-1.9
116 - P [c]	143.4 [63.0]	142.6 [≈7]	155.0 [7.5]	137.4 [66.5]	6.1

[a] Measured in C_6D_6 at 23 °C, coupling constants corresponding to $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$ are given in square brackets; [b] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = -6.4 [51.9, Si-Me], 24.8, 13.7 (Et), 134.6 [64.3, Si-CH=], 135.6 (=CH_2), 140.5 [6.0], 139.1 [6.2], 129.0, 128.7, 128.4, 126.9, 127.3, 126.1 (*i, i, o, o, m, m, p, p*, Ph); [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = -5.4 [49.5, Si-Me], 24.6, 14.5 (Et), 133.8 (=CH), 114.0 (H_2C=), 21.2 [46.2, Si-CH_2], 142.3 [6.7, *i*], 141.4 [5.9, *i*], 128.8, 128.7, 128.3, 127.6, 126.4 (*p*) 125.9 (*p*) (Ph).

Table 7.19. ^{13}C, ^{29}Si NMR data [a] for silols **119 - P** and **120 - P.**

	119a - P [b]	**119c - P** [c]	**120a - P** [d]	**120a´ - P** [e] [f]
$\delta^{13}C$(C-2)	143.5 [65.3]	142.1 [65.7]	139.9 [66.7]	137.9
$\delta^{13}C$(C-3)	154.6 [8.9]	156.0 [7.8]	155.0 [8.4]	155.5
$\delta^{13}C$(C-4)	144.9 [9.4]	143.7 [8.1]	143.2 [8.9]	145.0
$\delta^{13}C$(C-5)	133.4 [69.6]	135.9 [69.1]	135.7 [69.7]	135.8
$\delta^{13}C$(=CH)	133.5 [64.9]	132.1 [66.5]	133.3 [65.5]	132.7
$\delta^{13}C(H_2C=)$ [g]	135.0	137.1	135.9	136.1
$\delta^{29}Si$	-12.7	-10.4	-11.1	-11.7

[a] Measured in C_6D_6 at 23 °C, coupling constants $J(^{13}C,^{29}Si)$ are given in square brackets; [b] Other ^{13}C data: δ = 23.9, 13.5 (Et), 33.6, 33.0, 32.6, 28.9, 23.3, 23.0, 14.2, 14.2 (Bu); [c] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 13.4, 24.8 (Et), 140.4 [5.4], 138.9 [5.3], 129.0, 128.7, 128.6, 127.1, 127.4, 126.1 (*i, i, o, o, m, m, p, p,* Ph); [d] Other ^{13}C data: δ [$J(^{13}C,^{29}Si)$] = 24.0, 13.6 (Et), 34.5, 29.1, 23.3, 14.2 (Bu), 136.5 [5.4], 126.8, 125.7, 149.7, 33.5, 31.4 (*i, o m, p,* $C_{tert,}$ Me, 4-^{t}Bu-C_6H_4); [e] Other ^{13}C data: δ = 24.8, 13.6 (Et), 34.5, 31.1, 23.0, 14.1 (Bu), 136.7, 128.4, 125.5, 148.3, 33.1, 31.5 (*i, o m, p,* $C_{tert,}$ Me, 4-^{t}Bu-C_6H_4); [f] due to low concentration coupling constants were not determined; [g] $^2J(^{13}C,^{29}Si) \approx 5$ Hz.

DECLARATION/ERKLÄRUNG

Hereby I declare that this work has so far neither been submitted to the Faculty of Biology, Chemistry and Earth Sciences at the University of Bayreuth nor to any other scientific institution for the purpose of doctorate.

Furthermore, I declare that I have written this work by myself and that I have not used any other sources, besides those mentioned in this work.

Hiermit erkläre ich, dass diese Arbeit bisher von mir weder an der Fakultät für Biologie, Chemie und Geowissenschaften der Universität Bayreuth noch einer anderen wissenschaftlichen Einrichtung zum Zwecke der Promotion eingereicht wurde.

Ferner erkläre ich, dass ich diese Arbeit selbständig verfasst und keine anderen als die darin angegebenen Hilfsmittel benutzt habe.

Bayreuth, 31/10/2008

Ezzat Khan